Agricultural Research Institute
PUSA

THE EFFECT OF ACIDITY AND TIME IN THE ROASTING OF DEXTRINES

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A series of experiments were undertaken with a view to ascertaining what effect the degree of acidity and the time of roasting had upon the resultant dextrine. An ordinary powdered corn starch of the following composition was used in all of these experiments:

Moisture	10.48
Ash	.12
Protein	.44
Fiber	.21
Watersoluble	.48
Starch by difference	88.75
Acidity — cc. n/10 per 100 grs.	—18
Acidity — boiled	—20

The starch is placed in pans holding about 15 pounds each and put into kilns heated with steam coils to about 300° F. There are about twenty-six tiers of steam coils per kiln.

The methods used in obtaining my analytical data were the following:

1. *Watersoluble at 70° F.* Two grams dextrine were shaken for one hour with 50 cc. water in a 100 cc. graduated flask, which was then filled to the mark, shaken and allowed to stand for one hour, then filtered. 25 cc. of the clear filtrate were evaporated to dryness on steam bath in a tared glass evaporating dish and then dried in both at a temperature of 215° F. for one hour, cooled and weighed.

2. *Acidity* expressed in number of n/10 cc.

a. *Direct acidity:* One gram dextrine was distributed in 200 cc. hot water and titrated with n/10 NaOH using phenolphthalein as indicator.

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b. *Acidity of soluble:* 50 cc. of the watersoluble representing one gram of the dextrine were mixed with 500 cc. water and titrated with n/10 NaOH and phenolphthalein as indicator.

3. *Reducing Sugars* were determined volumetrically with Fehlings solution, which was so standardized that 5 cc. equalled .025 gram glucose. Five grams dextrine were shaken with water in a 200 cc. graduated flask, filled to the mark and allowed to stand for 4 hours with frequent shaking. Five cc. of Fehlings solution diluted with 10 cc. water was then titrated with the clear filtrate representing 2.5 grams dextrine in 100 cc. until the drop test (potassium ferrocyanide and acetic acid) showed complete reduction.

<div align="center">EXPERIMENT 1</div>

<div align="center">1000 LBS. OF STARCH WITHOUT ADDITION OF ANY ACID</div>

Test No.	Temp. of Kiln	Hours in Kiln	Acidity Direct cc. 1/10N NaOH	Acidity of Soluble cc. 1/10 N NaOH	Water Soluble	Water Insoluble	Reducing Sugars as Glucose	Appearance of Insoluble
1	308°F.	4	20	20	.28	99.72		Starchy
2	311	8	30	22	3.3	96.7		Starchy
3	312	12	40	20	13.2	86.8		Starchy
4	290	16	40	20	20.6	79.4		Starchy
5	310	20	40	20	37.2	62.8	Trace	Starchy
6	310	24	40	20	41.4	58.6		Starchy
7	310	28	50	35	45.9	54.1		Starchy
8	310	32	50	40	48.1	51.9		Starchy
9	312	36	55	40	72.6	27.4		Gummy
10	300	40	60	55	75.2	24.8	.84	Gummy
11	298	44	60	60	79.0	21.0		Gummy
12	300	48	60	60	77.6	22.4		Gummy
13	308	52	70	60	78.1	21.9		Gummy
14	294	56	55	60	83.2	16.8		Gummy
15	290	60	60	75	82.5	17.5	1.35	Gummy
16	292	64	60	75	77.8	22.2		Gummy
17	294	68	60	60	81.3	18.7		Gummy
18	302	72	60	70	81.7	18.3		Gummy
19	303	76	60	75	84.0	16.0		Gummy
20	310	80	60	80	82.7	17.3	1.47	Gummy
21	307	84	60	80	84.8	15.2		Gummy

EXPERIMENT I

100 LBS OF STARCH WITHOUT ADDITION OF ANY KIND

Test No	Temp of Kiln	Hours in Kiln	Acidity Direct cc 1/10 N NaOH	Acidity of Soluble cc 1/10 NaOH	Water Soluble	Water Insoluble	Reducing Sugars as Glucose	Appearance of Insoluble
22	315	88	70	80	86.2	13.8		Gummy
23	315	92	70	80	90.2	9.8		Gummy
24	306	96	70	100	92.5	7.5		Gummy
25	310	100	60	110	95.8	4.2	1.92	Gummy
26	312	104	50	80	98.2	1.8		Gummy
27	312	108	80	100	99.1	.9		Gummy
28	312	112	70	100	98.8	1.2		Gummy
29	313	116	80	100	96.5	3.5		Gummy
30	303	120	80	100	97.9	2.1	2.00	Gummy
31	313	124	80	100	98.2	1.8		Gummy
32	312	128	80	90	95.8	4.2		Gummy
33	310	132	80	80	94.1	5.9		Gummy
34	312	136	80	95	93.4	6.6		Very Gummy
35	304	140	100	100	92.5	7.5	2.43	Gummy
36	306	144	100	110	92.2	7.8		Gummy
37	312	148	90	95	91.2	8.8		Gummy
38	313	152	90	100	84.3	15.7		Gummy
39	310	156	100	100	80.3	19.7		Gummy
40	310	160	100	90	76.5	23.5	2.38	Gummy
41	306	164	100	95	75.6	24.5		Gummy
42	310	168	90	100	74.2	25.8		Gummy
43	311	172	90	100	76.0	24.0		Gummy
44	310	176	100	120	69.6	30.4		Gummy
45	312	180	100	100	69.0	31.0	2.27	Gummy
46	311	184	110	100	65.8	34.2		Gummy
47	312	188	100	110	65.7	34.3		Gummy
48	312	192	100	120	66.0	34.0		Gummy
49	312	196	110	110	65.1	34.8		Gummy
50	312	200	80	100	65.8	34.2	2.27	Gummy
51	312	204	110	120	65.2	34.8		Gummy
52	310	208	110	120	63.6	36.4		Gummy
53	310	212	120	120	64.7	35.3		Gummy
54	310	216	110	110	65.0	35.0		Gummy
55	310	220	110	120	64.8	35.2	2.08	Gummy

EXPERIMENT 1
100 LBS. OF STARCH WITHOUT ADDITION OF ANY ACID

Test No.	Temp of Kiln	Hours in Kiln	Acidity Direct cc. 1/10 N NaOH	Acidity of Soluble cc 1/10 NaOH	Water Soluble	Water Insoluble	Reducing Sugars as Glucose	Appearance of Insoluble
56	310	224	110	120	62.6	37.4		Gummy
57	311	228	120	120	61.0	39.0		Gummy
58	310	232	120	120	50.4	49.6		Gummy
59	312	236	120	120	50.2	49.8		Gummy
60	310	240	120	120	50.0	50.0	1.96	Gummy
61	310	244	120	120	49.6	50.4		Gummy
62	312	248	120	120	49.5	50.5		Gummy
63	310	252	120	120	48.9	51.1		Gummy
64	310	256	120	120	48.5	51.5		Gummy
65	310	260	120	120	47.0	53.0	1.75	Gummy

EXPERIMENT 2
1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, FOUR LBS. OF A 38° BE, ACID DILUTED TO 12° BE

Test No.	Temp. of Kiln	Hours in Kiln	Acidity Direct cc. 1/10 N NaOH	Acidity of Soluble cc 1/10N NaOH	Water Soluble	Water Insoluble	Reducing Sugars as Glucose	Appearance of Insoluble
1	298°F.	2	55.0	75.0	73.6	26.4		Starchy
2	297	4	55.0	75.5	96.8	4.0		Starchy
3	300	6	70.0	76.0	98.0	2.0		Starchy
4	298	8	85.0	78.5	99.2	.8		None
5	303	10	85.0	80.4	98.8	1.2	5.08	Gummy
6	298	12	95.0	80.4	98.4	1.6		Gummy
7	310	14	105.0	80.4	90.0	10.0		Gummy
8	300	16	100.0	90.0	90.0	10.0		Gummy
9	302	18	70.0	90.5	89.6	10.4		Gummy
10	298	20	70.0	96.4	90.4	9.6	3.72	Gummy
11	297	22	75.0	96.4	86.0	14.0		Gummy
12	297	24	67.5	95.6	86.0	14.0		Gummy
13	299	26	67.5	98.5	88.8	11.2	Very	Gummy
14	304	28	79.5	90.5	86.8	13.2		Gummy
15	295	30	79.5	112.0	86.4	13.6	3.25	Gummy
16	293	32	82.5	110.5	86.0	14.0		Gummy
17	302	34	82.5	112.0	84.4	15.6		Gummy
18	299	36	75.0	120.0	85.6	14.4		Gummy

<div align="center">EXPERIMENT 2</div>

1000 LBS. OF STARCH SOLIDIFIED WITH NITRIC ACID, FOUR LBS. OF
A 38° BE, ACID DILUTED TO 12° BE

Test No	Temp of Kiln	Hours in Kiln	Acidity Direct cc 1/10 N NaOH	Acidity of Soluble cc 1/10 NaOH	Water Soluble	Water Insoluble	Reducing Sugars as Glucose	Appearance of Insoluble
19	301	38	80.0	125.0	82.4	17.6		Gummy
20	304	40	75.0	144.0	82.0	18.0	2.89	Gummy
21	302	42	75.0	145.0	80.8	19.2		Gummy
22	300	44	90.0	145.0	80.0	20.0		Gummy
23	304	46	90.0	150.0	78.4	21.6		Gummy
24	300	48	90.2	150.0	75.2	24.6		Gummy
25	302	50	90.5	155.0	76.4	23.6	2.77	Gummy
26	300	52	90.0	155.0	74.2	25.8		Gummy
27	296	54	90.0	155.5	74.2	25.8		Gummy
28	302	56	90.2	160.0	74.1	25.9		Gummy
29	298	58	90.5	160.0	75.6	24.4		Gummy
30	298	60	105.0	160.0	75.0	25.0	2.67	Gummy
31	300	62	100.0	160.0	74.7	25.3		Gummy
32	308	64	80.0	160.5	74.7	25.3		Gummy
33	302	66	65.0	160.0	74.5	25.5		Gummy
34	297	68	70.0	160.5	74.0	26.0		Gummy
35	304	70	80.0	160.0	73.9	26.1	2.56	Gummy
36	305	72	85.0	160.0	73.0	27.0		Gummy
37	301	74	80.0	160.5	72.9	27.1		Gummy
38	301	76	75.0	170.0	72.4	27.6		Gummy
39	300	78	90.0	160.0	72.4	27.6		Gummy
40	299	80	85.0	160.5	72.1	27.9	2.39	Gummy
41[1]	330	82	85.0	160.5	69.7	30.3		Gummy
42	332	84	80.0	160.5	68.7	31.3		Gummy
43	340	86	90.0	160.0	66.0	34.0		Gummy
44	340	88	105.0	160.0	59.5	40.5		Gummy
45	340	90	120.0	160.0	52.0	48.0	2.34	Gummy
46	336	92	125.0	160.0	44.2	55.8		Gummy
47	340	94	120.0	160.0	40.0	60.0		Gummy
48	339	96	125.0	160.5	37.9	62.1		Gummy
49	336	98	130.0	160.5	36.7	63.3		Gummy
50	340	100	140.0	160.5	35.2	64.8	2.18	Getting Granular

[1]Temperature raised about 30° F at this point.

EXPERIMENT 2

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, FOUR LBS. OF
A 38° BE, ACID DILUTED TO 12° BE

Test No.	Temp. of Kiln	Hours in Kiln	Acidity Direct cc. 1/10 N NaOH	Acidity of Soluble cc. 1/10 NaOH	Water Soluble	Water Insoluble	Reducing Sugars as Glucose	Appearance of Insoluble
51	340	102	140.0	160.5	34.9	65.1	Getting	Granular
52	341	104	120.0	170.0	31.0	69.0	Getting	Granular
53	339	106	140.0	160.0	29.5	70.5	Getting	Granular
54	338	108	160.0	160.0	30.2	69.8		Granular
55	336	110	120.0	160.5	28.3	71.7	1.89	Granular
56	339	112	175.0	160.0	27.3	72.7		Granular
57	336	114	170.0	160.5	26.0	74.0		Granular
58	339	116	175.0	160.0	25.5	74.5		Granular
59	340		175.0	160.0	25.0	75.0		Granular
60	340	120	170.0	155.0	24.8	75.2	1.64	Granular
61	340	122	170.0	165.0	23.5	76.5		Granular
62	342	124	170.0	165.0	21.0	79.0		Granular
63	340	126	170.0	160.0	20.5	79.5		Granular
64	339	128	170.0	160.0	20.0	80.0		Granular
65	340	130	175.0	160.5	19.8	80.2	1.46	Granular

EXPERIMENT 3

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, EIGHT LBS. OF A
38° BE, ACID DILUTED TO 12° BE

Test No.	Temp. of Kiln	Hours in Kiln	Acidity Direct cc. 1/10N NaOH	Acidity of Soluble cc. 1/10N NaOH	Water Soluble	Water Insoluble	Reducing Sugars as Glucose	Appearance of Insoluble
1	300°F.	1	90.0	85.0	65.8	34.2		Starchy
2	298	2	85.0	125.0	86.9	13.2		Starchy
3	297	4	85.0	145.0	99.7	.3		None
4	300	6	100.0	200.0	99.5	.5		None
5	302	8	105.0	200.0	96.8	4.2	5.10	Gummy
6	310	10	110.0	200.0	84.1	15.9		Gummy
7	304	12	120.0	200.0	78.1	21.9		Gummy
8	312	14	125.0	200.0	73.5	26.5		Gummy
9	302	16	135.0	200.0	72.0	28.0		Gummy
10	300	18	135.0	200.0	71.8	28.2	3.56	Gummy
11	310	20	135.0	200.0	67.8	32.2		Gummy
12	297	22	135.0	200.0	70.0	30.0		Gummy

EXPERIMENT 3

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, EIGHT LBS. OF
A 38° BE, ACID DILUTED TO 12° BE

Test No.	Temp. of Kiln	Hours in Kiln	Acidity Direct cc. 1/10 N NaOH	Acidity of Soluble cc. 1/10 N NaOH	Water Soluble	Water Insoluble	Reducing Sugars as Glucose	Appearance of Insoluble
13	300	24	140.0	200.0	66.8	33.2		Gummy
14	308	26	140.0	200.0	64.9	35.1	Very	Gummy
15	300	28	180.0	200.0	63.7	36.3	2.78	Very Gummy
16	305	30	170.0	200.0	62.8	37.8		Gummy
17	302	32	170.0	200.0	63.0	37.0		Gummy
18	300	34	170.0	200.0	62.2	37.2		Gummy
19	310	36	170.0	200.0	59.3	40.7		Gummy
20	300	38	170.0	195.0	59.3	40.7	2.36	Gummy
21	302	40	170.0	180.0	60.8	39.2		Gummy
22	300	42	170.0	160.0	54.7	45.3		Gummy
23	310	44	170.0	180.0	55.6	44.4		Gummy
24	292	46	170.0	180.0	55.6	44.4		Gummy
25	306	48	200.0	180.0	52.1	47.9	2.08	Gummy
26	300	50	200.5	170.0	48.9	51.1		Gummy
27	309	52	200.0	170.0	47.8	52.2		Gummy
28	309	54	210.0	180.0	48.2	51.8		Gummy
29	300	56	215.0	165.0	47.0	53.0		Gummy
30	296	58	210.0	165.0	45.5	54.5	1.84	Gummy
31	310	60	210.0	165.0	45.4	54.6	Getting	Granular
32	302	62	205.0	180.0	42.2	57.8	Getting	Granular
33	295	64	210.0	180.0	42.2	57.8	Getting	Granular
34	310	66	200.0	185.0	41.5	58.5	Getting	Granular
35	298	68	205.0	185.0	42.1	57.9	1.75	Getting Granular
36	290	70	210.0	180.0	42.2	57.8	Getting	Granular
37	310	72	205.0	170.0	41.1	58.9	Getting	Granular
38	300	74	195.0	165.0	39.1	60.9	Getting	Granular
39	310	76	200.0	175.0	39.6	60.4	Getting	Granular
40	300	78	200.0	175.0	38.3	61.7	1.69	Granular
41	302	80	200.0	175.0	37.2	62.8		Granular
42	312	82	200.0	180.0	36.4	63.6		Granular
43	300	84	200.0	180.0	36.6	63.4		Granular
44	296	86	200.0	190.0	36.0	64.0		Granular
45	306	88	200.0	165.0	35.6	64.4	1.65	Granular

EXPERIMENT 3

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, EIGHT LBS. OF A 38 BE, ACID DILUTED TO 12° BE

Test No.	Temp of Kiln	Hours in Kiln	Acidity Direct cc 1/10 N NaOH	Acidity of Soluble cc 1/10 N NaOH	Water Soluble	Water Insoluble	Reducing Sugar as Glucose	Appearance of Insoluble
46	312	90	200.0	180.0	34.6	65.4		Granular
47	300	92	200.0	180.0	33.9	66.1		Granular
48	290	94	200.0	180.0	32.4	67.6		Granular
49	306	96	200.0	185.0	33.0	67.0		Granular
50	300	98	195.0	180.0	33.8	66.2	1.61	Granular
51	306	100	200.0	180.0	33.2	66.8		Granular
52	302	102	200.0	175.0	33.8	66.2		Granular
53	310	104	205.0	180.0	33.0	67.0		Granular
54	300	106	205.0	180.0	30.8	69.2		Granular
55	308	108	210.0	185.0	30.8	69.2	1.60	Granular
56	302	110	205.0	180.0	30.9	69.1		Granular
57	302	112	215.0	180.0	30.8	69.2		Granular
58	310	114	210.0	175.0	29.8	70.2		Granular
59	310	116	210.0	175.0	30.1	69.9		Granular
60	300	118	210.0	175.0	30.2	69.8	1.56	Granular
61	300	120	210.0	175.0	30.0	70.0		Granular
62	302	122	210.0	175.0	29.8	70.2		Granular
63	305	124	210.0	175.0	28.1	71.9		Granular
64	306	126	210.0	˙175.0	27.6	72.4		Granular
65	305	128	210.0	175.0	27.0	73.0	1.42	Granular

EXPERIMENT 4

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, TWELVE LBS. OF A 38° BE, ACID DILUTED TO 12° BE

Test No.	Temp of Ciln	Hours in Kiln	Acidity Direct cc 1/10 N NaOH	Acidity of Soluble cc 1/10 N NaOH	Water Soluble	Water Insoluble	Reducing Sugar as Glucose	Appearance of Insoluble
1	285	1	110	120	45.5	54.5		Starchy
2	295	2	100	100	67.5	32.5		Starchy
3	285	3	100	100	88.2	11.8		Starchy
4	286	4	90	100	92.0	8.0		Starchy
5	304	6	90	100	98.6	1.4	7.14	None
6	312	8	80	120	99.9	.1		None
7	312	10	120	130	98.4	1.6		None

EXPERIMENT 4

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, TWELVE LBS. OF
A 38° BE, ACID DILUTED TO 12° BE

Test. No.	Temp. of Kiln	Hours in Kiln	Acidity Direct cc. 1/10 N NaOH	Acidity of Soluble cc. 1/10 N NaOH	Water Soluble	Water Insoluble	Reducing Sugar as Glucose	Appearance of Insoluble
8	311	12	120	130	96.3	3.7		Gummy
9	313	14	130	130	93.7	6.3		Gummy
10	313	16	120	140	94.0	6.0	4.54	Gummy
11	308	18	120	140	92.5	7.5		Gummy
12	303	20	120	145	90.2	9.8		Gummy
13	298	22	140	160	90.1	9.9		Gummy
14	312	24	140	150	89.0	10.0		Gummy
15	295	26	150	160	87.2	12.8	4.49	Gummy
16	308	28	150	160	87.5	12.5		Gummy
17	295	30	160	160	86.7	13.3		Gummy
18	290	32	160	170	82.2	17.8		Gummy
19	306	34	160	160	82.4	17.6		Gummy
20	310	36	170	160	80.4	19.6	4.44	Gummy
21	304	38	180	150	79.8	20.2		Gummy
22	308	40	180	160	79.6	20.4		Gummy
23	290	42	160	150	77.3	22.7		Gummy
24	302	44	160	150	76.2	23.8		Gummy
25	315	46	180	150	72.7	27.3	4.20	Gummy
26	310	48	180	150	73.0	27.0		Gummy
27	307	50	180	160	71.5	28.5		Gummy
28	301	52	180	160	70.2	29.8		Very Gummy
29	300	54	180	150	64.9	35.1		Very Gummy
30	306	56	180	155	61.1	38.9	3.73	Very Gummy
31	308	58	170	160	61.2	38.8		Very Gummy
32	308	60	180	160	60.4	39.6		Very Gummy
33	298	62	180	160	59.8	40.2		Very Gummy
34	308	64	180	160	59.0	41.0		Very Gummy
35	302	66	180	160	56.7	43.3	3.50	Very Gummy
36	306	68	180	160	57.0	43.0		Very Gummy
37	296	70	180	160	53.2	46.8		Very Gummy
38	310	72	180	160	52.1	47.9		Very Gummy
39	310	74	180	160	49.5	50.5		Very Gummy
40	306	76	180	160	49.1	50.9	3.39	Very Gummy

EXPERIMENT 4

1000 LBS. OF STARCH ACIDIFIED WITH NITRIC ACID, TWELVE LBS. OF
A 38° BE, ACID DILUTED TO 12° BE

Test No	Temp of Kiln	Hours in Kiln	Acidity Direct cc 1/10 N NaOH	Acidity of Soluble cc 1/10 N NaOH	Water Soluble	Water Insoluble	Reducing Sugar as Glucose	Appearance of Insoluble
41	303	78	190	160	47.3	52.7		Very Gummy
42	301	80	190	155	49.2	50.8		Very Gummy
43	299	82	190	155	50.1	49.9		Very Gummy
44	302	84	190	155	50.3	49.7		Very Gummy
45	307	86	190	155	48.2	51.8	3.20	Getting Granular
46	309	88	190	160	47.8	52.2		Getting Granular
47	308	90	200	160	45.6	54.4		Getting Granular
48	297	92	190	155	43.7	56.3		Getting Granular
49	310	94	190	155	45.1	54.9		Getting Granular
50	312	96	200	160	43.8	56.2	3.12	Getting Granular
51	300	98	200	155	43.2	56.8		Getting Granular
52	300	100	195	155	42.7	57.3		Getting Granular
53	304	102	200	160	40.9	59.1		Getting Granular
54	309	104	200	160	40.4	59.6		Getting Granular
55	307	106	200	150	37.4	62.6	2.71	Getting Granular
56	305	108	200	150	36.4	63.6		Getting Granular
57	307	110	210	155	39.6	60.4		Getting Granular
58	310	112	210	155	40.4	59.6		Getting Granular
59	308	114	200	155	40.7	59.3		Getting Granular
60	310	116	200	160	39.7	60.3	2.50	Getting Granular
61	310	118	220	155	39.6	60.4		Granular
62	310	120	210	155	40.0	60.0		Granular
63	307	122	222	155	39.5	60.5		Granular
64	312	126	220	160	38.9	61.1		Granular
65	310	126	220	165	39.0	61.0	2.46	Granular

The temperatures in these experiments were not controlled as closely as might have been desired and the necessity of taking periodic samples caused a lowering of the temperature in the kiln of 10° to 15° F.; it took 15 to 20 minutes to raise to the initial temperature.

The most significant features shown in the experiments are the gradual and continuous rise in acidity and the increase of

soluble and reducing sugars to a certain point, followed by their gradual decline.

The fluctuations in the individual results can probably be attributed to an uneven operation in the kiln itself and a corresponding difference in the sample taken, due to a more rapid rate of conversion among the middle tiers of coils than at the top and bottom.

PREPARATION OF CHEMICALLY PURE GLUCOSE FROM THE COMMERCIAL PRODUCTS

By H. F. Bauer

Waukegan, Illinois

When chemically pure glucose has to be prepared in the laboratory, Soxhlet's method is generally used. Soxhlet starts with cane sugar, which he inverts with concentrated hydrochloric acid, to which alcohol has been added. The glucose crystallizes out after about 10 days standing, when the mother liquor containing all of the frutase is removed on suction filter. Then the crystals are washed several times with 90% alcohol and finally recrystallized from methylalcohol.

The author has succeeded in making chemically pure glucose from the various commercial grades of sugars made by hydrolysis of starch. The three types used were "anhydrous sugar" (92.8 glucose), "80 sugar" (80.1% glucose), and "70 sugar" (71.2% glucose); all of these sugars contain a certain amount of moisture, mineral matter and dextrines. 80 and 70 sugars contain all the mother liquor, while the anhydrous sugar is nearly free from mother liquor, which has been removed by mechanical means. To remove this mother liquor from the raw glucose crystals a preliminary washing with methylalcohol is necessary. The sugars were ground up so finely that they could pass through a No. 20 mesh sieve; as 70 and 80 sugars contain a large amount of moisture, about 20% and 11% respectively, it is first necessary to cut these sugars in small pieces and dry them until most of the moisture content is driven out, then they can be easily ground.

The sugars are placed in a percolator with a cotton plug in its bottom covered with a small piece of filter paper; the percolator is so arranged that vacuum suction can be applied.

The sugars are now steeped with their weight of methylalcohol at ordinary room temperature, first for 12 hours when the alcohol

is removed by suction, then with a new portion of methylalcohol for 6 hours. For 70 and 80 sugars, a third washing must be applied.

The washed sugar crystals are dissolved in a small amount of distilled water, and when dissolved, alcohol is added. The solution is heated in steam bath, and then filtered to remove the insoluble impurities.

Amount of water and alcohol necessary for 100 grams of sugar taken in work:

	70 Sugar	80 Sugar	Anhydrous Sugar
Water	25cc.	30cc.	40cc.
Alcohol	100cc.	125cc.	140cc.

The solutions are now concentrated to syrupy consistency and methylalcohol added. For each 100 grams of sugar taken in work use:

For 70 sugar	50cc.
For 80 sugar	60cc.
For anhydrous sugar	70cc.

Let the solution stand for about one-half hour, until crystallization starts, then add again the same amount of methylalcohol and stir every 5 minutes to prevent hard incrustation of crystals on the dish; pour the mass into a percolator, let stand for 12 hours and remove mother liquor, using vacuum suction; steep for 15 minutes with 25cc. methylalcohol for each 100 grams of sugar taken in work; remove the alcohol, using suction; wash 3 times in this way. Dry the crystals in vacuum at a temperature not exceeding 90° C.

Such prepared glucose showed the following analysis:

Moisture	none
Ash	.005
Nitrogenous matter	none
Dextrine	none
Specific rotatory power	
$[a] D 20 =$	52.6
Melting point	143-146° C.

An ash-free glucose was obtained by recrystallization from methyl-alcohol.

I obtained the following yield from the three various types of commercial sugars taken in work:

Anhydrous sugar	65%
80 sugar	50%
70 sugar	32%

THE INFLUENCE OF TEMPERATURE ON HYDRATION OF AND ABSORPTION OF ALKALI BY RE-GENERATED CELLULOSE

By Clayton Beadle and Henry P. Stevens, M.A., Ph.D., F. I. C.

That cellulose has the power of absorbing[1] or condensing various dissolved substances when immersed in solutions of the same is known, although little has been done to investigate the mechanism of such reactions. It is well known that the power of hydration exercised by cellulose is largely influenced by the presence of caustic soda as well as by the "condition" or kind of cellulose submitted to the treatment.

Practically no work has been done upon the behaviour of any particular form of regenerated cellulose towards dissolved substances in promoting hydration and absorption. J. F. Briggs' investigations are interesting in this connection (Der Papier Fabrikant May 1910). On the other hand, work of a similar character has been done with cotton for the purpose of studying the question of mercerisation.

The object of this communication is primarily to describe work we have undertaken to determine the influence of temperature as affecting the behaviour of caustic soda of different concentrations towards a specific form of regenerated cellulose. The form of regenerated cellulose chosen by us was a monofil of uniform diameter made by the cuprammonium process in a factory under our supervision. This monofil had a denier of 360, it showed a breaking strain of 1.6 grams per denier and an elongation at break of 20% on the original length.

Lengths of the above in the form of small skeins weighing 0.200 grams were immersed in 20 cc. of the different solutions experimented with for periods of 30 minutes. The skeins were then taken out and weighed after the careful removal of any

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[1]We are probably dealing with the phenomenon known as *adsorption*. We have not, however, used this term, as we are not satisfied that the action is entirely a physical one.
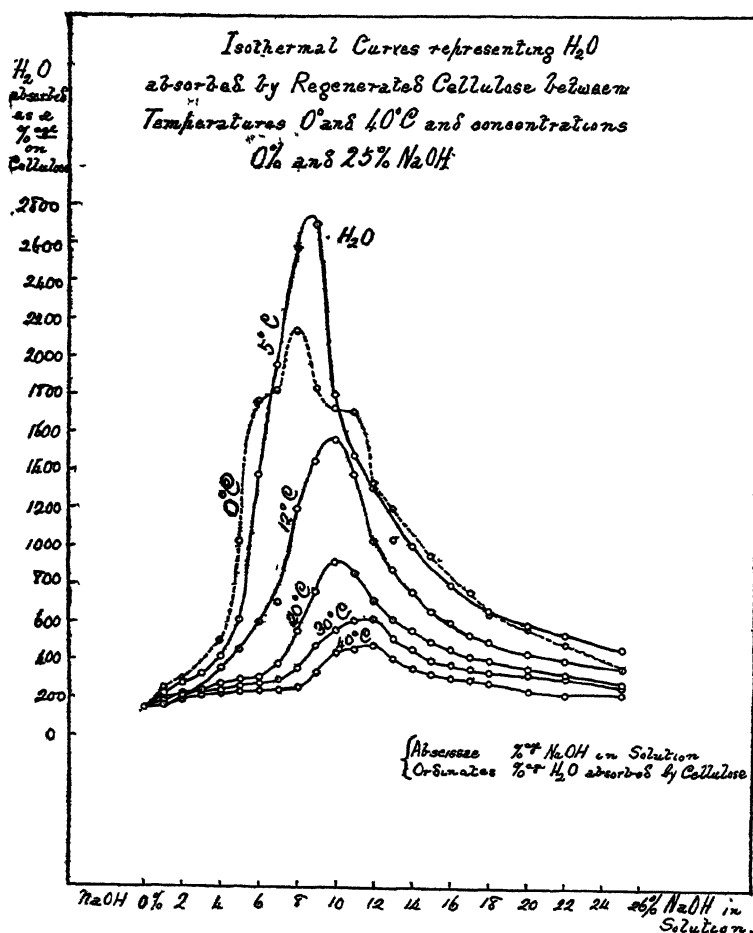
DIAGRAM 1

surface liquid. The total amount of alkali was determined in each by titration. The "hydration" figure was obtained by deducting the amount of NaOH found from the gain in weight. Both the hydration and NaOH absorption figures were calculated to a percentage on the original weight of cellulose. Before we settled upon a 30 minutes' immersion we made a number of trials, varying the period of immersion, and came to the conclusion that 30 minutes

Isothermal Curves representing NaOH
absorbed by Regenerated Cellulose between
Temperatures 0° and 40°C and concentrations
0% and 25% NaOH.
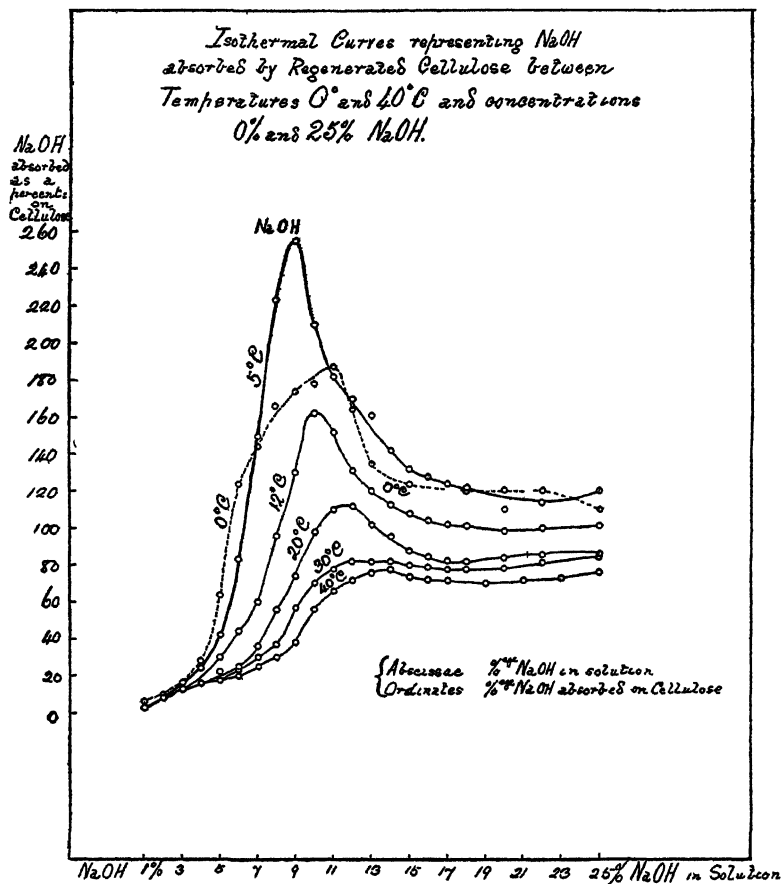
DIAGRAM 2

would best suit our purpose. It is our intention to make a further
series of experiments for the purpose of determining the time
required for equilibrium under different conditions.

The following figures show how far the results agree when re-
peated:

	NaOH Absorption	
NaOH in Bath	1st Series at 5° C.	2nd Series at 5° C.
4.0%	24	23
5.0%	42	43
6.0%	83	83

Had we taken precautions to read the temperatures more accurately the repetition figures would have been sufficiently close to be expressed to the first place of decimals. In the results recorded we have, however, omitted decimals and given the nearest round number. It must be understood that the results are in some measure determined by the conditions under which the thread has been manufactured. We therefore found it necessary to satisfy ourselves that the monofil used for the experiments was uniform in every particular.

TABLE A

NaOH in bath	HYDRATION Cellulose = 100					NaOH ABSORPTION Cellulose = 100				
	at 5° C.	at 12° C.	at 20° C	at 30° C.	at 40 C	at 5° C.	at 12° C.	at 20° C.	at 30°C.	at 40°C
1.0%	217	160	182	197	167	3	3	3	3	3
2.0%	279	210	217	212	192	8	8	8	8	8
3.0%	324	237	241	231	216	16	13	14	14	14
4.0%	426	358	280	237	224	24	16	16	18	16
5.0%	615	456	300	260	230	42	30	22	19	17
6.0%	1380	600	310	278	238	83	44	25	23	20
7.0%	1960	710	380	300	240	150	60	36	30	25
8.0%	2576	1200	562	360	261	224	96	56	37	30
9.0%	2699	1450	758	485	338	256	130	74	57	38
10.0%	1800	1558	920	558	440	210	162	98	70	56
11.0%	1483	1380	861	610	458	182	152	110	78	66
12.0%	1310	1030	719	620	480	170	131	112	82	72
13.0%	1200	885	620	519	412	161	120	102	82	76
14.0%	1003	760	558	460	360	142	113	96	82	78
15.0%	798	665	500	400	334	132	108	88	80	74
16.0%	762	600	458	385	310	128	104	84	79	72
17.0%	715	540	420	360	300	124	102	82	78	71
18.0%	658	500	400	340	280	122	101	82	78	70
20.0%	590	438	360	330	240	110	98	84	78	72
22.0%	540	400	325	310	220	114	99	86	81	73
25.0%	461	360	280	260	220	120	101	86	84	76

Table A gives figures for hydration and NaOH absorption when the regenerated cellulose in question is immersed in so-

lutions of from 1% to 25% NaOH and at temperatures of 5°, 12°, 20°, 30°, and 40°C.   As the results for 0°C. are of a somewhat different order from those of the foregoing we have given the figures for these separately in Table B.

TABLE B

NaOH in Bath	Hydration at 0° C. Cellulose=100	NaOH absorption at 0° C. Cellulose=100
1.0%	254	6
2.0%	300	10
3.0%	331	14
4.0%	502	28
5.0%	1031	64
6.0%	1766	. 124
7.0%	1825	144
8.0%	2135	166
9.0%	1831	174
10.0%	1727	178
11.0%	1707	188
12.0%	1336	164
13.0%	1036	134
15.0%	962	122
18.0%	650	120
20.0%	577	120
22.0%	490	120
25.0%	365	110

Diagram 1, plotted from Tables A and B, gives us the isothermal hydration curves and Diagram 2, similarly plotted, the isothermal soda (NaOH) absorption curves.   To distinguish observations at 0°C. from the others they are plotted in broken line.   It will be noticed that in the case of Diagram 1 the hydration for 0.0% NaOH is given, *i. e.*, gain in weight on immersion in water alone for 30 minutes.   There is comparatively little difference for hydration in water alone for the different recorded temperatures.

Leaving out of consideration for the time being the observations at 0°C. and taking the case of Diagram 1, it will be noticed that for any given temperature   (between 5°C. and 40°C.) a maximum hydration takes place, these maxima being greater the
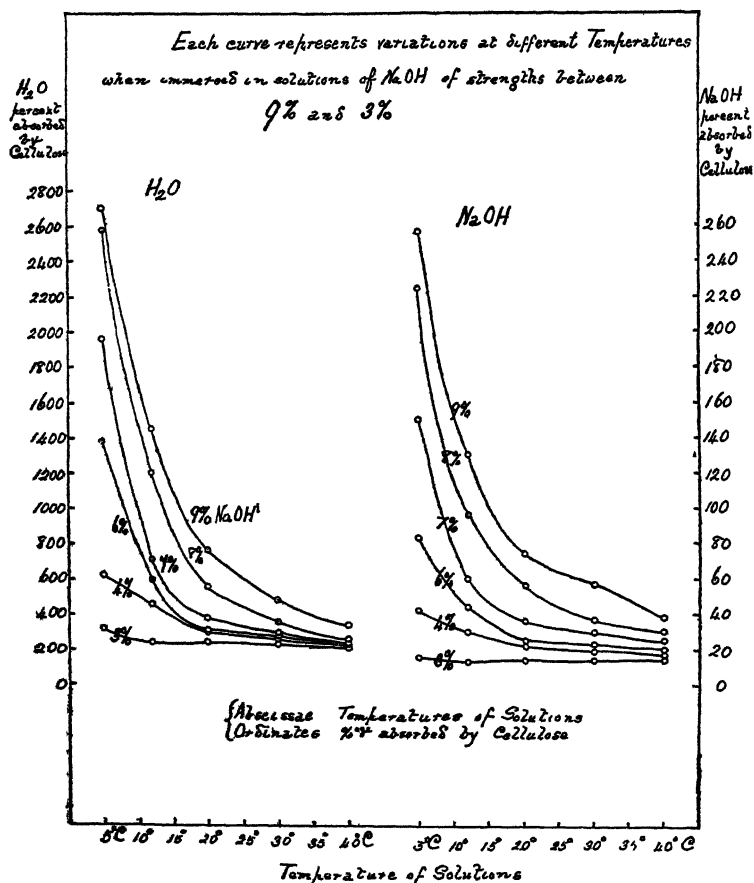
DIAGRAM 3

lower the temperature. At or near each maximum the differ-
ence per degree of temperature is greater, the lower the temper-
ature. There is also a maximum at 0°C. but it falls below max-
imum for 5°C.

Although the maxima cannot be definitely placed without a
greater number of observations in the neighbouring percent-
ages, these maxima may be stated to occur as follows:
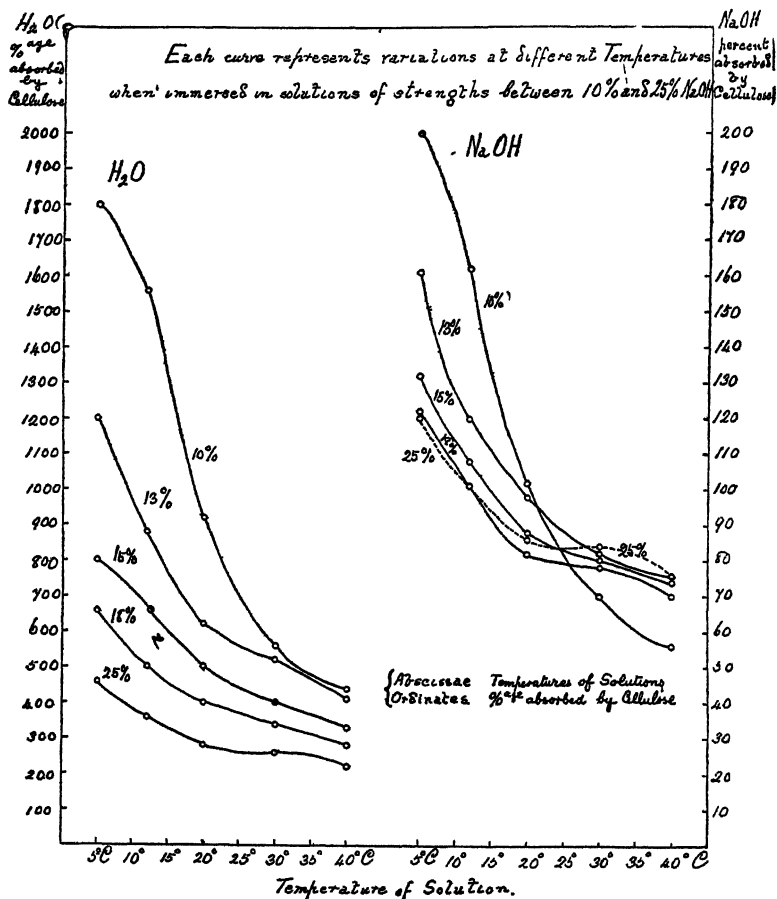
DIAGRAM 4

°C.		Solution	
At 5	in about	9%	NaOH
At 12	in about	10%	NaOH
At 20	in between	10 and 11%	NaOH
At 30	in between	11 and 12%	NaOH
At 40	in between	11 and 12%	NaOH

The same observations apply to the NaOH absorption. Here we have the following maxima:

°C.			Solution	
At	5	in about	9%	NaOH
At	12	in about	10%	NaOH
At	20	in between	11 and 12%	NaOH
At	30	in between	12 and 14%	NaOH
At	40	in about	14%	NaOH

The maxima for hydration and NaOH absorption therefore take place at greater concentrations as the temperature rises.

At 0°C. it will be observed that although we get a maximum hydration (at 8% NaOH) the curve is nothing like so regular. Also, the maximum soda absorption is at 11%. The behaviour at 0°C. is therefore of a different order from that of the other recorded temperature except that a maximum is reached.

Diagram 3 illustrates the effects of different temperatures upon hydration and NaOH absorption, in which each curve represents a different strength of mother liquor.

Diagram 4 is plotted in a similar manner to Diagram 3 but for percentages of mother liquor between 10% and 25% NaOH. Observe the difference in the character of the curves and their relationship to one another as concentration increases above 9% NaOH.

It will be observed that in 3% to 9% the hydration and NaOH absorption curves bear a fairly close resemblance to one another. If, in the process of swelling, the solution in which the cellulose is immersed were absorbed en masse and without change of composition, then the two sets of curves would be exactly similar to one another. The extent to which these two sets of curves differ from one another indicates the change of composition as the result of absorption (*i. e.* adsorption).

Table C is calculated for the purpose of showing how far the solution contained in the swollen mass differs in composition from that of the mother liquor. In the first column we have the strength of the mother liquor and under each of the temperature columns we have the actual strength (NaOH %) as contained in the swollen mass calculated to W/V basis in order to be comparable with column 1. After each figure is given the difference figure (+ or −) indicating the difference between the strength of the mother liquor and that absorbed by the swollen mass.

TABLE C

Strength of Soda solution used NaOH %	Corresponding strength of Soda solution (NaOH%) as contained in swollen mass. Against each figure is placed the "difference" figure (+ or −)										
	0°C.		5°C.		12°C.		20°C.		30°C.		40°C.	
1.0	2.2	+1.2	1133	+0.3	1188	+0.8	1.6	+0.6	1.5	+0.5	1.7	+0.7
2.0	3 0	+1.0	2.8	+0.8	3.6	+1.6	3.4	+1.4	3.5	+1.5	3.8	+1.8
3.0	3.9	+0.9	4.5	+1.5	5.9	+2.9	5.2	+2.2	5.4	+2.4	5.7	+2.7
4.0	5.0	+1.0	5.2	+1.2	4.0	0.0	5.1	+1.1	6.6	+2.6	6.2	+2.2
5.0	5.5	+0.5	6.0	+1.0	5.8	+0.8	6.4	+1.4	6.4	+1.4	6.4	+1.4
6.0	6 2	+0.2	5.4	−0.6	6.4	+0.4	7 4	+1.4	7.1	+1.1	7.3	+1.3
7.0	6.8	−0.2	6.6	−0.4	7.2	+0.2	8.6	+1.6	9.5	+2.5	8.6	+1.6
8.0	6.7	−1.3	7.4	−0.6	7.0	−1.0	8.3	+0.3	9.9	+1.9	9.3	+1.3
9.0	8.0	−1.0	7.8	−1.2	7.6	−1.4	8.2	−0.8	9.5	+0.5	9.0	0.0
10.0	8.5	−1.5	9.4	−0.6	8.6	−1.4	8.7	−1.3	9.7	−0.3	10.1	+0.1
11.0	9.0	−2.0	9.9	−1.1	9.0	−2.0	10.1	−0.9	10.1	−0.9	11.2	+0.2
12.0	9.4	−2.6	10.2	−1.8	10.0	−2.0	11.9	−0.1	10.4	−1.6	11.5	−0.5
13.0	10.7	−2.3	10.6	−2.4	10.7	−2.3	12.4	−0.6	12.0	−1.0	13.5	+0.5
14.0	...	...	11.0	−3.0	11.5	−2.5	12.9	−1.1	13.2	−0.8	15.2	+1.2
15.0	10.1	−4.9	12.5	−2.5	12.3	−2.7	13.0	−2.0	14.3	−0.7	15.4	+0.4
16.0	...	...	12.7	−3.3	12.9	−3.1	13.5	−2.5	14.6	−1.4	15.9	−0.1
17.0	...	...	13.0	−4.0	13.7	−3.3	14.1	−2.9	15.1	−1.9	16.1	−0.9
18.0	13.5	−4.5	13.6	−4.4	14.4	−3.6	14.6	−3.4	15.8	−2.2	16.7	−1.3
20.0	14.8	−5.2	13.6	−6.4	15.5	−4.5	16.0	−4.0	16.1	−3.9	19.3	−0.7
22.0	16.6	−5.4	15.0	−7.0	16.7	−5.3	17.5	−4.5	17.3	−4.7	20.4	−1.6
25.0	19.4	−5.6	17.3	−7.7	18.4	−6 6	19.7	−5.3	20.1	−4.9	20.7	−4.3

It will be observed that at all recorded temperatures for low concentrations the absorbed solution is more concentrated than the unabsorbed or surrounding mother liquor, but at each temperature a point of concentration is reached at which the solution absorbed by the swollen hydrated cellulose synchronises in strength with that of the surrounding solution. This point, as will be observed, is somewhere about 6% for 0°C. and between 8 and 9% for 20°C., between 9 and 10% for 30°C.—in fact, there is a perfectly clear indication that the synchronising strengths advance in concentration as the temperature rises and that, within certain temperature limits, they bear some relation to, if they do not exactly correspond with, the strengths at which maxima occur such as are shown in Diagrams 1 and 2.

Table C also makes clear the point that, after reaching strengths at which the absorbed and external liquids synchronise in com-

H_2O and NaOH adsorption-changes in Regenerated
Cellulose when immersed in 8% NaOH solution & heated from
-5°C to 45°C
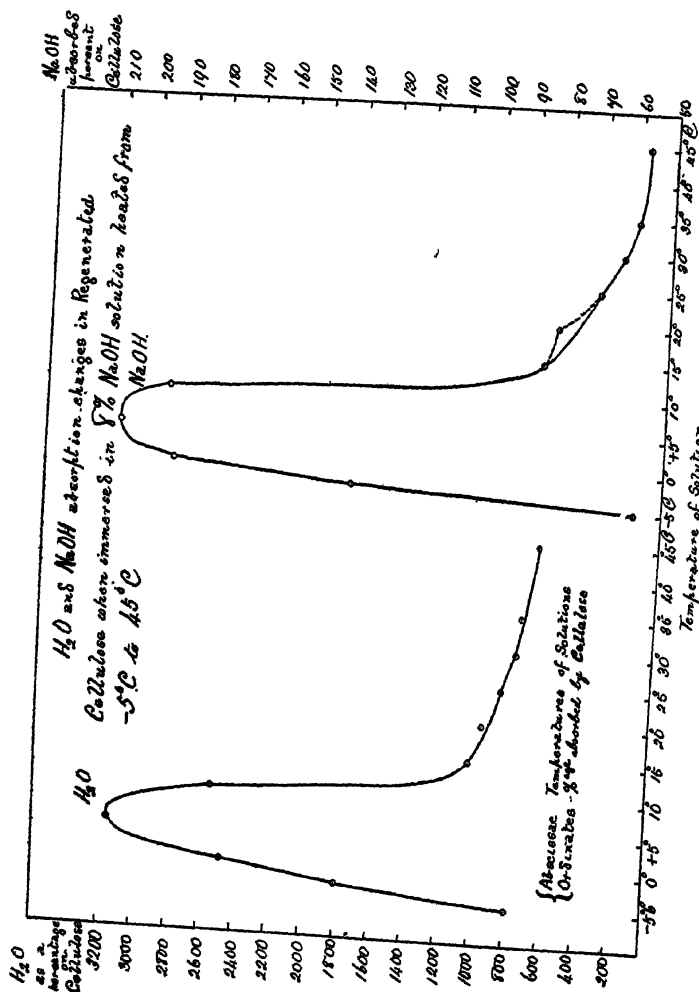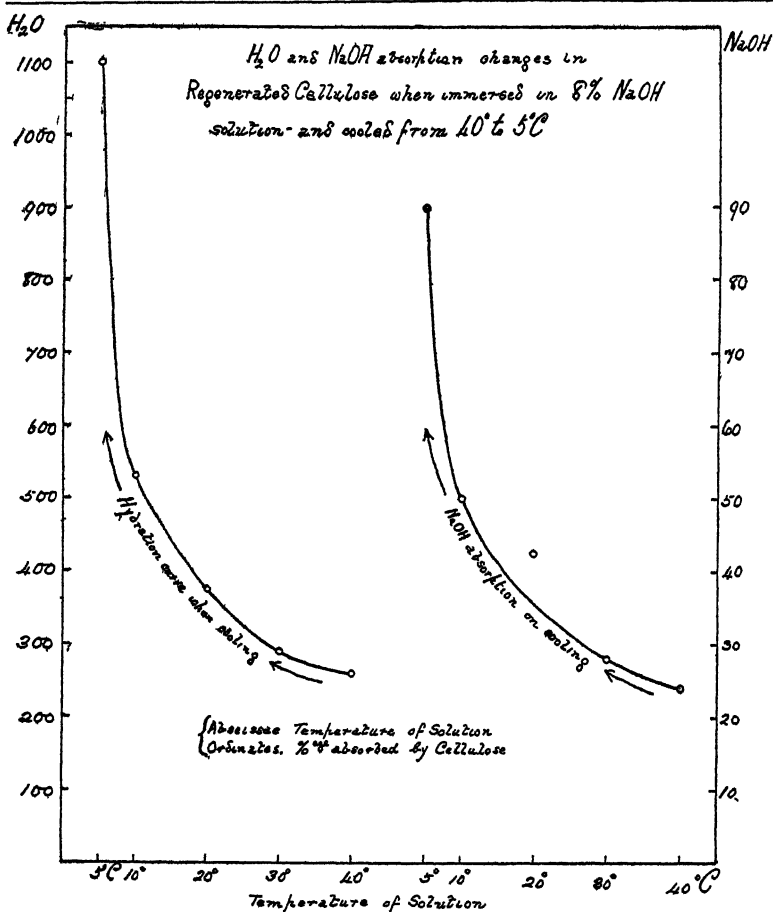
DIAGRAM 5

DIAGRAM 6

position as the concentration advances, the "difference" figure increases. Thus, at 0°C. and 9% NaOH the difference figure is in the neighbourhood of −1; at a concentration of 25% NaOH the difference figure is −5.6, and at 5°C. (for 25% NaOH) the difference figure is greater still (i.e. −7.7). It will be observed that the order in which the temperatures show the greatest "differences" at high concentrations (25%) corresponds with the order of maximum hydration and soda absorption as shown on Dia-

grams 1 and 2. The results rather indicate that the mother liquor concentration point of maximum hydration for any given temperature (Diagrams 1 and 2) corresponds somewhat with the point at which there is osmotic equilibrium (Table D), i.e., the point at which no difference exists between the composition of the absorbed liquid and the solution which surrounds it. If the two sets are not the same one set follows the other. Furthermore, that the temperature which gives in concentrated solution the greatest "difference" is also the temperature at which the greatest hydration is observable as a maximum and greatest differences in the hydration as the result of change of temperature.

In the results already recorded each figure was based on a test on an independent sample treated for 30 minutes. In order to see whether the same sample could be changed from one state of hydration to another, a sample similar to that used in the foregoing was placed in an 8% NaOH solution, the solution being slowly heated and the sample removed at intervals. The state of hydration is found to vary according to the temperature in the same manner as in the foregoing results (Diagram 3). One cannot, however, obtain exactly the same figures in this way without arresting the temperature at each point for say 30 minutes to establish equilibrium before removal of each sample.

For the purpose of investigating the influence of changing temperatures below 0°C., skeins were immersed in an 8% solution at −5°C. slowly heated to 45°C. and at intervals the hydration and soda absorption determined. In this case a number of the skeins were placed in the same mother liquor and taken out one at a time at convenient intervals as the temperature changed. 8% NaOH mother liquor was chosen for this and the foregoing as being the concentration which was most likely (judging from Diagrams 1 and 2) to show the greatest differences at different temperatures. It will be observed that in the neighbourhood of 5°C. we have a maximum and the curves on either side of the maximum appear to correspond very closely with one another until a temperature of about 14°C. is reached (see Diagram 5).

In Diagram 6 we have a similar set of experiments in which the cooling effect is observed between 40°C. and 5°C. The actual figures are without doubt influenced by the time of heating and

the time of cooling respectively. As the rate of change of temperature was fairly rapid, taking not more than one hour for each set of tests, equilibrium was not established at the time each sample was removed. Diagram 5 shows, however, that a maximum comes about at 5°C. for 8% NaOH, above which and below which for a few degrees there is rapid dehydration.

We have investigated the influence of common salt (NaCl) upon the hydration and NaOH absorption. If the regenerated cellulose is exposed under similar conditions to the foregoing (at 20°C., as recorded in Table A), to varying strengths of soda solution, which solution also contains 20% of NaCl, then the hydration varies only slightly compared with that containing no salt, increasing between 4% and 13% NaOH in mother liquor, above which latter strength it slightly diminishes. At its maximum hydration (at 5° C.) it is never more than about one-tenth of the hydration to be noticed in the absence of the NaCl.

The amount of NaCl absorbed by the regenerated cellulose has also been carefully determined. This remains fairly constant (at 5° C.) between 4% and 13% NaOH in mother liquor; at higher concentrations it diminishes.

The NaOH absorption, however, is a progressively increasing figure (at 5° C.) until one employs a mother liquor of 18% NaOH, after which it remains fairly constant up to a mother liquor of 25%. As the caustic soda is increased in strength from 15% to 25% (at 5° C.) in the presence of a constant proportion of NaCl (20%) the hydration diminishes, the NaCl absorption diminishes, whereas the NaOH absorption, if anything, increases. We have similarly investigated sodium sulphate. It is therefore evident that the addition of other soluble salts profoundly alters the hydration and the NaOH absorption, not only in degree but in kind. The influence of NaCl and other salts in this connection is being systematically studied and it is our intention that the same shall form a communication upon the subject when the work is further advanced.

In a case where the hydration figure was 1927 and the NaOH absorption 108 we added absolute alcohol and found the hydration diminished to 975 and the NaOH absorption to 36. Thinking that these results might in some way be connected with surface

tension, we tried the effect of adding 2% of soap in caustic soda solutions of 8%. We found no difference whatever in the figures for hydration and NaOH absorption as the result of the addition of the soap.

It is not our intention in this communication to arrive at an explanation of the results so far obtained, our object being merely to place them on record. We hope to offer an explanation at a later stage.

We were led to study these changes whilst investigating the manufacture of artificial silk and horsehair by what is known as the soda process of coagulation, which process has formed the subject of a large number of patents. The results herein recorded help to differentiate materially two classes of patents, one in which the thread is coagulated in soda alone and the other in soda plus salt. The results also serve to indicate the enormous importance of observing exact conditions in the manufacture of such products, particularly in regard to concentration and temperature of coagulating baths.

In conclusion we desire to thank Miss A. Borrowman and Mr. J. J. Watt for their assistance in the experimental work.

THE PAPER MAKING QUALITIES OF THE HEDYCHIUM CORONARIUM

By Clayton Beadle and Henry P. Stevens
London, England

This plant belongs to the order *Zingiberaceæ* and its order in the vegetable kingdom lies between the *Musaceæ* and *Cannaceæ*. It is described by Lindley as a plant with tuberous roots, herbaceous stems, clasping leaves and a terminal spicate inflorescence. It is distinguished by its handsome and fragrant flowers, especially the species *Hedychium Coronarium*.

The *Hedychium Coronarium*, like all members of the order, possesses an aromatic odor. The herb is tropical and found in Southern Asia as well as in South America. Several plants belonging to the same order are found in Ceylon and in the West Indies, also in parts of China. In some cleared lands where it has been planted it spreads like a carpet, by means of its rhizomes, to the exclusion of all other vegetable growth, and reaches a height of from one to two metres. Its relation to the *Musas* led us to think that perhaps it might be of service for textile purposes. We have this matter now under consideration, but the purpose of this communication is to describe only its paper-making qualities.

Photomicrograph[1] Fig. 1 shows a transverse section of two fibre-vascular bundles stained with Hæmatoxylin (Kleinenberg's formula), magnification 280 diameters. Photomicrograph Fig. 2 shows ultimate fibres, stained with chloride of zinc iodide magnification 125. Treating the transverse section with chloride of zinc iodide, the xylem portion of the fibro-vascular bundle is colored bright yellow, showing lignification, but when the fibre undergoes chemical treatment and is treated with the same reagent it is merely colored a pale violet. It will be noticed that, mixed with the fibres as prepared for paper making, there are a number of simple spiral vessels. We made a chemical analysis of the dried specimens as received with the following results:

[1]The photomicrographs are prepared by John Christie, F.R.M.S.

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A. Whole stem as gathered.
B. Whole stem after passing through crushing-rollers.

	A	B
Moisture.......................	9.7%	11.2%
Ash	4.5	4.8
Cellulose......................	43.0	48.0
Extracted by chemical treatment	42.8	36.0
	100.0	100.0
Cellulose air dry on air dry allowing for losses	41.0%	44.0%

Raw material in the form of B is conveniently treated by boiling with 5% of soda at a pressure of three to five atmospheres. On washing this material, the yield of boiled product including all the fibrous constituents of the plant is 60%. The peculiar characteristics of the pulp are largely due to the presence of the oval cells of the pith, which is included in the above 60%. If these are removed by washing, the yield of fibre proper is 50% of unbleached material on the raw weight.

We discovered that the pith cells, which can be retained or not, according to requirements, possess very peculiar qualities. If taken alone, the unbleached cells when dried down go to a horny mass which can only be broken with very great difficulty with a hammer, and are softened only with difficulty when boiled in soda. If retained in the paper, they give it parchment-like properties to an extraordinary degree. They also render the paper ink bearing without the addition of any sizing material. Banana also can be made to possess ink-bearing qualities in the "waterleaf" form but it offers certain difficulties when run over the Fourdrinier paper machine which the *Hedychium* is free from. On the other hand, the paper made from *Hedychium* from which the cells are removed is of a soft nature and of medium strength but that in which the cells are retained, as will be seen, gives higher "breaking lengths" than any manila paper that we have so far had the opportunity of examining. The oval cells, therefore, "parchmentize," strengthen and size the sheet.
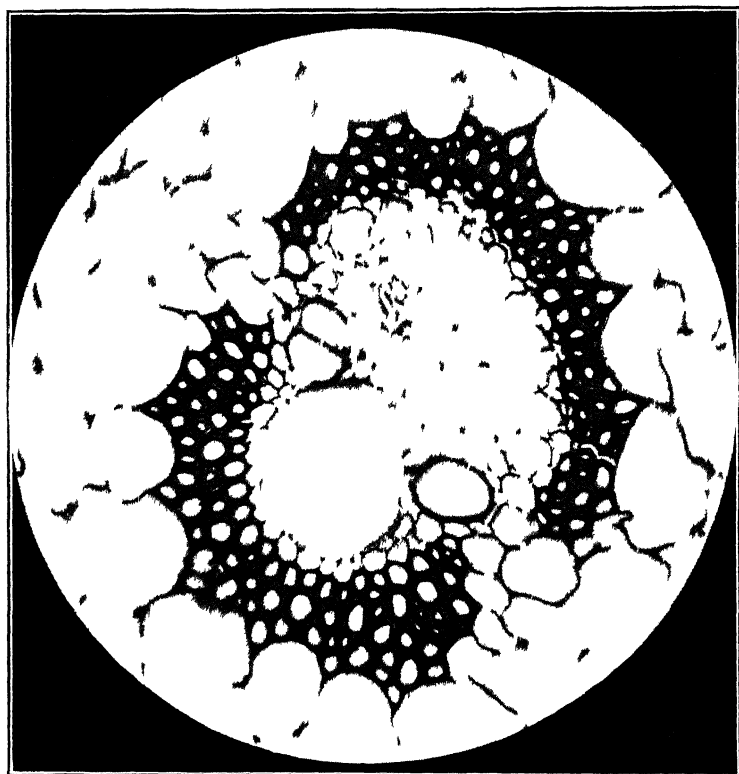
Y S F V Bundli Hidychium Coronarium   x 280
(Section Starrld Hamatoxylin)

The pulp, after boiling in soda and beating, if examined under the microscope in the presence of chloriodide of zinc shows:

(a) Oval cells stained blue.

(b) Long wide fibres something like chemical wood, stained blue.

(c) Numerous shorter and solid looking fibres, stained yellow.

(d) Small epidermal cells attached to one another, stained yellow.

Length of Fibres. Table A gives the results of measurements under the microscope of

1. Hedychium fibres, unbleached, not beaten.

2. Hedychium bleached, not beaten.

3. Hedychium cells washed through 70-mesh wire, measured lengthwise.

4. Hedychium cells washed through 70-mesh wire, measured crosswise.

5. Best strong thick manila cable paper.

6. Ditto, thin.

TABLE A

	1		2	3		4		5		6	
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
	1.76	5.29	1.57	.10	.16	.08	.10	2.07	3.73	3.28	3.08
	1.83	1.57	3.14	.18	.12	.06	.08	3.98	3.36	2.03	4.29
	2.90	2.75	3.93	.18	.18	.12	.12	3.15	2.33	3.22	2.14
	2.80	1.22	.80	.06	.14	.04	.10	2.94	4.47	3.25	4.31
	1.62	2.16	1.72	.18	.16	.06	.08	4.07	1.13	1.48	2.08
	6.82	4.07	2.19	.12	.08	.06	.06	1.38	1.67	2.00	1.18
	2.50	2.42	2.87	.20	.08	.10	.06	3.19	2.35	2.61	2.65
	2.35	2.52	3.08	.12	.16	.10	.08	3.13	1.73	4.37	3.62
	1.34	1.31	3.30	.12	.10	.08	.08	1.35	5.22	4.04	2.70
	2.14	2.84	3.03	.18	.12	.08	.12	3.54	2.19	1.84	3.70
Mean	2.61	2.61	2.56	.144	.132	.078	.088	2.84	2.83	2.81	2.97
Mean	2.61		2.56	.138		.083		2.835		2.89	

Mean of 3 and 4 = 0.110 mm.

It will be observed that the mean size of the cells, taking the mean of the two directions, is 0.11 mm., or less than 1/20 of the length of the fibres which measure 2.58. It can be understood, therefore, that such small particles as the oval cells will pass through a 70-mesh sieve of the washing drum, the holes of which would be about 0.2 mm., but the same sieve would of course retain the fibres proper. It will be observed also that the mean length of the fibres of the longest and strongest manila papers, which is about 2.85 mm., is only slightly in excess of that of the *Hedychium* fibre but, as will hereafter be seen, the *Hedychium*, on account of the peculiar nature of the fibres and the cells, is capable of producing a stronger and in many respects more serviceable paper. Moreover, the smallness of the *Hedychium* cells in comparison with the fibres enables the cells to fill the interstices between the fibres. Moreover, these cells, being of a flocculent, sticky and glutinous nature, act as a natural sizing material. We mechanically separated and weighed the cells and fibres with the following results:

The actual amount of fibre proper and cells in *Hedychium* unbleached paper, the cells of which have been entirely retained, we find to be as follows:

Cells................ 17.3%
Fibre................ 82.7%

When the pulp is completely bleached so as to produce a white paper, the proportion by weight of cells and fibres in the finished paper is as follows:

Cells.................. 14%
Fibre.................. 86%

We have made several trials of this material on the paper machine. The beaten fibre, especially that containing the pith cells, when left in an unbleached condition, has an extremely greasy feel, enough to lead one to suppose that it would only part with its water with very great difficulty on the paper machine. Unlike most greasy feeling pulp, however, the water drains from the machine wire with great rapidity. We have seen the pulp on the wire of the paper machine on five or six occasions. In one case

ULTIMATE FIBRE HIDYCHIUM CORONARIUM ✕ 125
(CHLOR ZINC IODINE)

TABLE B

	A	B	C	D	E	F	G	H	I	J	K	L	M
1. Thickness in mm.	.062	.088	.064	.070	.10	.080	.10	......	.110	.173	.066	.148	.077
2. Substance. Demy lbs.	8.9	14.1	9.2	10.0	19.9	13.3	20.2	......	20.9	31.6	27.1	26.3	11.4
Strength in lbs. per inch width													
3. Machine direction	8.6	26.9	13.5	18.8	37.0	21.5	44.6	......	41.3	42.7	24.3	73.8	12.88
4. Cross direction	6.0	13.3	6.7	9.5	27.3	18.5	29.4	......	17.2	26.2	14.7	25.0	12.00
5. Mean	7.3	20.1	10.1	14.2	32.2	20.0	37.0	......	29.2	34.4	19.5	49.4	12.44
Corrected to 0.1 mm. thick													
6. Machine direction	13.9	30.6	20.4	26.9	37.0	27.0	44.6	......	37.5	25.2	36.8	49.3	16.7
7. Cross direction	9.7	15.1	10.2	13.6	27.3	23.2	29.4	......	15.6	15.4	22.3	17.0	15.6
8. Mean	11.8	22.9	15.3	20.3	32.2	25.1	37.0	......	26.5	20.3	29.5	33.1	16.1
9. Breaking length in metres	6633	8018	8303	10083	8078	9381	9039	7950	6318	3204	5424	6286	7045
Stretch													
10. Machine direction	3.0%	3.8%	4.1%	3.8%	5.4%	4.6%	6.0%	2.8%	4.8%	4.2%	4.6%	4.4%	4.5%
11. Cross direction	7.0%	10.2%	8.8%	8.2%	9.2%	9.5%	9.8%	7.8%	10.1%	7.4%	7.2%	13%	8.6%
12. Mean	5.0%	7.0%	6.5%	6.0%	7.3%	7.1%	7.9%	5.3%	7.5%	5.8%	5.9%	8.7%	6.6%
Final permanent elongation as measured after break													
13. Machine direction	2.6%	3.4%	3.2%	3.2%	2.6%	2.5%	3.4%	......	1.8%	2.0%	......	1.8%	1.8%
14. Cross direction	5.2%	6.8%	7.0%	6.6%	6.4%	6.5%	6.8%	......	3.0%	4.2%	......	8.6%	4.8%
15. Mean	3.9%	5.1%	5.1%	4.9%	4.5%	4.5%	5.1%	......	2.4%	3.1%	......	5.2%	3.3%
Bursting Strain (Eddy)													
16. Lbs. per sq. in.	14	24.2	11.3	13.7	......	......	......	......	32.0	44.4	28.6	63.6	21.1
17. Corrected to 0.1 mm.	17.2	20.7	14.8	17.8	......	4.50	55.0	......	29.1	26.0	43.4	43.0	27.4

TABLE B. — *Continued.*

Grease Proof Tests	A	B	C	D	E	F	G	H	I	J	K	L	M
18. Turpentine test	{ Not proof	{ Not proof	{ Not proof	Proof	Proof	Proof	Proof	……	……	……	Proof	……	……
19. Cold butter test	{ Not proof	{ Not proof	{ Not proof	Proof	Proof	Proof	Proof	……	……	……	Proof	……	……
20. Hot butter test	{ Not proof	{ Not proof	{ Not proof	Proof	Proof	Proof	Proof	……	……	……	Proof	……	……
21. Blister test	{ Not proof	{ Not proof	{ Not proof	Proof	Proof	Proof	Proof	……	……	……	Proof	……	……

EXPLANATION OF HEADINGS TO TABLE B

Column   lbs.

A. Hedychium ½ bleached   8 Large Post "Waterleaf."
B. Hedychium ½ bleached 12 Large Post "Waterleaf."
C. Hedychium ½ bleached   8 Large Post rosin sized.
D. Hedychium ½ bleached   9 Large Post rosin and gelatine sized.
E. Hedychium bleached white, beaten in Hollander.
F. Hedychium bleached white, beaten in Hollander.
G. The same as E and F but unbleached.
H. Pure manila paper as officially tested at the Berlin Testing House, 14th September, 1904.
I. Kraft B, supposed to be the best English make.
J. The best Kraft supplied by Messrs. James Spicer & Son, 16th November, 1911.
K. Vegetable parchment supplied by Messrs. James Spicer & Sons, retailed at 4d per lb.
L. English Matte pure manila imulating paper, thick.
M. English Matte pure manila imulating paper, thin.

The above papers A to D were boiled in 5% soda and washed in breaker so as to remove a great proportion of the cells.
E, F, G contain all the cells but no sizing material.

when making a parchment paper, we observed that the water left the wire quickly after the apron — in fact, in one-quarter of the space taken by a wood-pulp paper made on the same machine at the same speed.   This argues in favor of the possibility of comparatively fast running on the paper machine, in spite of the greasy feel and the parchment-like qualities.

For the purpose of making a comparison of papers producible from the *H. Coronarium* with papers with which it is likely to come into competition, we carried out a number of tests as to strength, breaking strain, elongation, bursting strain and greaseproof qualities.   These are contained in Table B.

We draw attention to this fibre as we believe it may become of great industrial importance to the paper trade.   Where circumstances are congenial to its growth, the plant spreads to the exclusion of all other vegetable growth by means of its rhizomes, so that it can be harvested at least once a year, producing a heavy crop. It is an easy pulp to manipulate.   It is capable of producing a paper of exceptional strength and can be worked either bleached or unbleached.   The fact that the paper in its natural state, without the addition of any materials whatever, can be made to possess greaseproof and self-sizing qualities is a point of commercial importance.

Our thanks are due to Mr. John Christie for his kindness in preparing the photomicrographs.

COMPOSITION OF COMMERICAL GLUCOSE

By Arthur' P. Bryant

Clinton, Iowa

It is well known that commercial glucose, or corn syrup, is a very complex material, containing a large number of intermediate products in the cleavage or hydrolysis of the starch molecule, ending with dextrose. In ordinary practise it is quite customary to determine the reducing value of the glucose and call it dextrose, while the remaining organic matter is called dextrin. There is present, however, a certain amount of maltose, and various methods have been proposed to determine the proportions of dextrose and maltose, which need not be referred to at this time further than to say that they usually ignore the possible presence of other reducing matter than dextrose and maltose.

When commercial glucose is fermented with yeast there is invariably found a residue which still shows a considerable reducing power towards Fehling solution. This may be due to the incomplete action of the yeast on the dextrose and maltose, or to the presence of some substance like the gallisin of Schmidt and Coblenz, or the isomaltose of Fischer, or it may be due to some of the less complex dextrins which, undoubtedly, have a reducing action on Fehling solution. It is unnecessary at this place to give a *résumé* of the literature on this subject, which is very considerable in amount. Moreover, it was not so much the object of these experiments to gain light on the exact nature of this residual product as to get some idea of the relative amounts of dextrose and maltose.

Plan of the experiments. Three series of experiments were carried on with commercial glucose from different sources. In two of these series 20 grams of glucose was made to 100 cc. and in the other series 10 grams to 100 cc. In the twenty per cent solutions brewers' yeast was used. This was washed free from all reducing matter, freed from excess moisture and used in the proportion of two grams per 100 cc. solution and the fermentation continued until there was no further lessening of the reducing

value, the temperature being maintained at 30–35° C. A little more yeast was then added and the test allowed to stand twenty-four hours longer, although in no instance was there evidence of further activity. The ten per cent solutions were fermented with two grams compressed yeast per 100 cc. until there was no further drop in the reducing value, and likewise let stand twenty-four hours more with fresh yeast.

The fermented solutions were then filtered and analyzed in the same way as the unfermented solutions. The determinations made were solids, reducing value, optical activity, ash, and in many cases nitrogen. Similar determinations were made upon a filtered solution of water and yeast with four per cent alcohol, which had been kept at the same temperature as the glucose solutions while the latter were fermenting. The results of the test on the blank showed that the yeast imparted no reducing material or optically active substance to the solution. The amount of solids in solution was extremely small, averaging not over one or two hundredths gram per 100 cc., most of which was apparently nitrogenous in character.

Analytical methods. Solids in the unfermented and fermented solutions were determined by drying on sand in vacuo at the temperature of boiling water. The reducing value was determined volumetrically by Fehling solution, the glucose solution being made to such strength that its reducing value was practically equivalent to that of a one per cent dextrose solution when this was practicable. However, the difference in reducing power for different concentrations appears to be very slight for dextrose and not very pronounced for maltose solutions, as will be seen from the table following. The specific rotary power was determined in a sugar scale polariscope. The sensitiveness of this instrument, unfortunately, was not sufficiently great to warrant fine distinctions being made in the results of different experiments. All determinations of reducing value and specific rotary power have been calculated to dry matter in the tables beyond.

Relative reducing power of solutions of dextrose and maltose. A chemically pure dextrose prepared by repeated crystallization of commercial dextrose from alcohol was dissolved in water in the proportion of 1.0 gram, .5 gram, .25 gram, and .1 gram, respec-

tively, per 100 cc., and the amount of dextrose in the solution determined volumetrically. Similar solutions were made with a so-called chemically pure maltose, with the exception that the highest concentration was 2 grams per 100 cc. and the lowest .25 grams per 100 cc. The relative reducing power of this sugar as well as its specific rotary power showed that it was not a strictly pure maltose, but no attempt was made to purify it.

A comparison of the amounts of reducing sugar in the various solutions actually present as compared with amounts found is shown below:

| Sugar in 100 cc. | | Sugar Found | Sugar Found As Maltose |
Dextrose Grams	Maltose Grams	Dextrose Equivalent Grams	(Factor .62) Grams
1.000	. . . . .	1.000	. . . . .
1.000	. . . . .	1.000	. . . . .
.500	. . . . .	.500	. . . . .
.500	. . . . .	.500	. . . . .
.500	. . . . .	.496	. . . . .
.250	. . . . .	.248	. . . . .
.250	. . . . .	.248	. . . . .
.100	. . . . .	.100	. . . . .
.100	. . . . .	.100	. . . . .
. . . . .	2.000	1.116	1.800
. . . . .	2.000	1.116	1.800
. . . . .	1.000	.571	.921
. . . . .	1.000	.571	.921
. . . . .	.500	.272	.439
. . . . .	.500	.270	.435
. . . . .	.250	.136	.219
. . . . .	.250	.136	.219

Completeness of fermentation. In order to compare the completeness of fermentation under the conditions of these experiments ten per cent solution of sucrose, dextrose and maltose were made and treated in exactly the same way and at the same time as the experiments with glucose. The dextrose contained a little moisture which was not removed for these tests. Results are as follows:

10% Solution	Sucrose %	Dextrose %	Maltose %
Solids, % by volume,	10.00	9.50	9.96
Solids after fermentation,	.07	.04	.04
Residual reducing value as dextrose,	.01	.02	.03
Nitrogen,	.015	....	....

A blank solution run at the same time showed .01% solids. The .03% reducing value of maltose at the end of the fermentation would be equivalent to .05% actual maltose still unfermented.

Dialysis of sugar solutions. Experiments were run in which glucose and the unfermented residue were submitted to dialysis in running water in vegetable parchment tubes. In order to determine the length of time necessary to dialyze dextrose and maltose solutions, ten per cent concentrations were made and dialyzed until the solution in the parchment showed no further reducing value. At the same time ten per cent solutions of two commercial dextrins were submitted to dialysis. The results were as follows:

	Dextrose Solution Grams	Maltose Solution Grams
Solids in 100 cc.,	9.500	9.850
Solids remaining in 12 hours,	.450	1.650
24 hours,	.036	.770
36 hours,	.011	.390
48 hours,	.000	.210
60 hours,	.....	.028
72 hours,	.....	.000

	"C Dextrin"	"British Gum"
Solids in 100 cc.,	9.65	9.32
Solids remaining in 24 hours,	8.17	8.55
Solids remaining in 48 hours,	7.55	7.90
Per cent dialyzed,	21.8	15.2
Dextrose equivalent at start,	.980	.240
Dextrose equivalent at end,	.507	.186
Per cent dialyzed,	48.2	22.5
Dextrose equivalent material dialyzed,	22.5%	3.8%
Dextrose equivalent material not dialyzed,	6.8%	2.4%

From the above results it will be seen that the dialysis of dextrose and maltose should be practically complete in forty-eight hours and that there is evidently a considerable dialysis of either dextrose, maltose, or reducing dextrins in the case of commercial dextrins.

Description of samples. Samples A to I were secured from various parts of the country and represent the product of various companies manufacturing glucose. All but the last sample, I, were made from the starch of maize, while sample I was manufactured from potato starch and imported. Samples J to M are another representative line of glucose samples as put out by four different concerns. Samples N, O and P represent separate steps in the hydrolysis of starch in the manufacture of glucose. Sample N was taken from the "converter" when the hydrolysis had been going on about one-third the full required time. Sample O represents the same "conversion" after about two-thirds the time had elapsed, while sample P was taken from the finished "boil" after hydrolysis had been checked by removal of pressure and the neutralization of acidity.

Samples Q to T were treated with compressed yeast, the glucose being identical with that used in J to M respectively. It will be observed that fermentation, although complete for that kind of yeast, was decidedly less than with brewers' yeast.

Results of the experiments. The following table gives the analytical results obtained in these tests. The solids were for the most part determined by drying on sand as already stated, and in nearly all cases results thus determined were corroborated by determination of the refractive index and the per cent Brix. The "dextrose equivalent" is the reducing value calculated as dextrose. Percentages are all by volume, or grams per 100 cc.

In the following table is shown the computed dextrose value (K) of the dry material before and after fermentation, also the specific rotary power (S_d) of the dry material before and after. The last four columns of the table show the computed composition of the glucose.

The determination of the unfermented residue in glucose suffices for the estimation of the proportions of dextrose and maltose upon the supposition that no other reducing material is fermented.

RESULTS OF ANALYSIS OF GLUCOSE SOLUTION BEFORE AND AFTER FERMENTATION AND DIALYSIS

MATERIAL	In Original Solution					In Fermented Solution					After Dialysis Unfermented Solution		
	Solids in 100 cc.	Dextrose Equivalent	Reading on Sugar Scale[1]	Nitrogen	Ash	Solids in 100 cc.	Dextrose Equivalent	Reading on Sugar Scale[2]	Nitrogen	Ash	Solids in 100 cc.	Dextrose Equivalent	Reading on Sugar Scale[2]
	grams	%	°	%	%	grams	%	°	%	%	grams	%	°
Glucose A	16.63	7.94	64.5	.003	.08	7.86	1.49	68		.06			
B	16.54	8.01	64.0	.003	.06	8.00	1.51	70		.06			
C	16.60	8.09	63.5	.003	.06	8.05	1.52	72		.06			
D	16.30	6.84	65.0	.002	.10	9.05	1.51	82.5		.10			
E	16.34	7.31	65.0	.002	.12	8.50	1.50	80		.12			
F	16.04	7.00	64.5	.002	.07	8.50	1.49	77.5		.07			
G	16.30	7.25	64.5	.005	.08	8.75	1.52	81		.08			
H	16.48	7.25	65.0	.005	.06	8.87	1.54	82.5		.06			
I	17.24	8.70	64.5	.001	.07	7.80	1.56	68.5		.07	5.15	1.20	46.2
Glucose J	16.88	7.96	64.5	.002	.10	9.17	1.80	85.0	.015	.10	6.30	1.44	55.0
K	16.71	6.72	69.0	trace	.10	10.03	1.81	97.5	.008	.11	5.25	1.36	45.7
L	17.05	7.40	68.5	.003	.10	9.50	1.76	90.5	.011	.10	4.84	1.14	43.5
M	17.05	8.50	65.2	.003	.08	8.44	1.75	77.5	.009	.10	8.36	1.45	82.3
N	20.61	6.01	92.6	.005	.10	14.26	2.08	73.0[1]	.015	.11	6.46	1.20	60.0
O	20.32	7.40	86.0	.005	.10	13.06	2.23	63.5[1]	.020	.10	4.68	1.15	43.0
P	20.55	9.40	77.6	.005	.10	11.20	2.19	104.0	.020	.11	.10		
Sucrose	10.00					.04	.01		.006				
Dextrose	9.50	9.50				.04	.02		.006				
Maltose	9.96	5.68				.04	.02		.006		.21	.12	
Dextrin A	9.65	.98									7.55	.51	
Dextrin B	9.32	.24									7.90	.19	
Glucose Q (J)	8.32	3.92			.05	5.49	1.42						
R (K)	8.30	3.33			.05	5.78	1.30						
S (L)	8.32	3.60			.05	5.44	1.23						
T (M)	8.33	4.14			.04	5.24	1.45						

[1] Direct, 100 mm. tube.   [2] Direct, 200 mm. tube.

Thus: Let D equal dextrose, M equal maltose, K equal reducing value as dextrose, F equal amount fermented and .62 the relative reducing value of maltose as compared with dextrose.

$$\text{Then } D + .62\,M = K$$
$$\underline{D + M = F}$$
$$\text{Subtracting } .38\,M = F - K$$

The composition of the unfermentable material cannot be determined as definitely as that of the fermentable. If, as is altogether probable, the reducing value of the unfermentable residue is due to a reducing dextrin, it would certainly be difficult to determine in actual composition. On the other hand, if it is due to isomaltose or gallisin, we are confronted by the fact that there is a very large amount of this material, although hydrolysis has not been carried very far. Moreover, an attempt to obtain a characteristic osazone of this unfermentable residue failed, no osazone separating in either the hot or cold solution. With commercial glucose the osazone of both dextrose and maltose was separated without difficulty. In the unfermentable residue of grape sugar, however, Bryant and Miner found a material giving an osazone which strongly suggested the presence of some such material as gallisin or isomaltose.

Discussion of results. Among the interesting points brought out by these tests is the fairly approximate agreement between the dextrose value and the total fermentable sugars, the average of tests A to P showing 44.1% for the dextrose equivalent and 45.9% for the fermentable matter. In other words, for all practical purposes the determination of the reducing value of the glucose as dextrose gives a fairly close measure of the total fermentable matter.

There is much less variation in the proportion of maltose than of dextrose and the lower the total amount of reducing sugars the less the dextrose until in the early stages of hydrolysis (see Experiment N) there is no dextrose at all. Maltose appears to be formed first and then inverted with formation of dextrose.

There is a marked uniformity in the reducing value of the unfermentable residue which strongly suggests that there is an ap-

COMPOSITION OF DRY SUBSTANCE OF COMMERCIAL GLUCOSE

MATERIAL	ORIGINAL MATERIAL DRY SUBSTANCE		UNFERMENTED RESIDUE DRY SUBSTANCE				COMPUTED COMPOSITION			
	Dextrose Value K	Specific Rotary Power S_i	Dextrose Value K_1	Dextrose Value in Terms Original Material K	Specific Rotary Power S_i	Proportion Original Solids Fermented	Dextrose	Maltose	Dextrins	Ash
	%	°	%	%	°	%	%	%	%	%
Glucose A	47.7	134	18.9	8.9	152	52.7	16.1	36.6	47.0	.3
B	48.4	136	18.9	9.2	153	51.6	19.0	32.6	48.1	.3
C	48.7	134	18.9	9.2	153	51.5	19.9	31.6	48.2	.3
D	42.3	139	16.7	9.3	162	44.5	14.2	30.3	54.9	.6
E	44.7	139	17.7	9.2	154	48.0	12.5	35.5	51.3	.7
F	43.6	141	17.5	9.3	160	47.0	14.6	32.4	52.6	.4
G	44.4	140	17.4	9.3	164	46.3	16.8	29.5	53.2	.5
H	44.0	139	17.3	9.3	164	46.2	15.9	30.3	53.4	.4
I	50.5	132	19.4	9.0	155	54.8	19.8	35.0	44.8	.4
Glucose J	47.2	132	19.6	10.7	160	45.7	21.5	24.2	53.8	.5
K	40.2	143	18.0	10.8	168	40.0	12.1	27.9	59.5	.5
L	43.4	139	18.5	10.3	164	44.3	14.8	29.5	55.3	.4
M	49.8	132	20.7	10.3	159	50.5	21.6	28.9	49.1	.4
N	29.2	155	14.6	10.1	177	30.8	0.0	30.8	68.8	.4
O	36.4	146	17.1	11.0	168	35.7	8.6	27.1	63.9	.4
P	45.7	130	19.6	10.6	160	45.5	18.1	27.4	54.1	.4
Average 16 tests	44.1					45.9				
Sucrose	0.0	67				99.9				
Dextrose	100.0	53				99.8				
Maltose	57.0	130				99.7				
Glucose Q (J)	47.1		25.9	17.1		34.0	12.7	21.3	65.5	.5
R (K)	40.1		22.5	15.7		30.4	9.6	20.8	69.1	.5
S (L)	43.3		22.4	14.7		34.6	2.5	32.1	65.0	.4
T (M)	49.7		27.7	17.4		37.1	12.4	24.7	62.5	.4

proximately constant proportion of the dextrins having an action
on Fehling solution, maltose being formed by hydrolysis of these
simpler dextrins at approximately the same rate that the more
complex dextrins are broken down into the simpler forms.

The longer the action of the acid on the starch and its cleavage
products, the more maltose is inverted. A high degree of conver-
sion is, therefore, indicative of a relatively large dextrose content,
and a low degree of conversion of a relatively small dextrose con-
tent, the maltose remaining practically the same in all cases.[1]

Experiments with fermentation of dextrose and maltose indicate
that the action of the yeast is practically complete. Failure to
obtain an osazone from the unfermented residue bears out this
supposition.

The four experiments with ordinary compressed yeast give re-
sults strongly indicative of incomplete fermentation, although no
further action took place on a longer treatment with fresh yeast.
No comparisons on fermentation of pure dextrose and maltose
by means of compressed yeast were made. The results of these
experiments, Q to T, are, therefore, not worthy of comparison
with those of the other experiments.

Experiments on the dialysis of glucose show that the most of
the reducing sugars and also much of the dextrin passed through
the membrane. Treatment of the undialyzed residue with phenyl-
hydrazine gives dextrosazone and maltosazone and shows that at
the end of two days there still remained some of these sugars which
had not dialyzed. Dialysis of the unfermentable residues showed
a reduction in the total solids but no great change in the relative
reducing values. Experiments on the dialysis of dextrose and
maltose show that in two days all of the former and practically
all of the latter sugar had been removed from the solution.

SUMMARY

The determination of the dextrose equivalent of the glucose
gives a close measure of the total amount fermentable, but the

[1] Experiments by the writer and C. S. Miner indicate, however, that in
grape sugar, where hydrolysis has been carried on to a much greater degree
than in glucose, all the maltose has been changed to dextrose.

larger part of the fermentable sugar is maltose, which is fairly constant in amount, averaging roughly 30% of the dry substance.

Hydrolysis of starch under conditions existing in the manufacture of commercial glucose appears to yield a nearly constant amount of reducing dextrins and maltose, while the dextrose varies widely in amount according to the "degree of conversion."

A STUDY OF THE UNFERMENTABLE RESIDUE IN HYDROLITIC PRODUCTS OF STARCH

By A. P. Bryant and C. S. Miner

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In the hydrolysis of starch it has long been recognized that there is frequently found an unfermentable but reducing residue, which differs from pure dextrose or maltose or other sugar on the one hand and from the dextrins on the other. The first work of any especial importance was done by Schmitt and Coblenz (Ber. 17–1000–and 2464), who obtained from this unfermentable residue a substance which they called gallisin. They determined its properties but by methods which were open to criticism. Scheibler and Mittelmeier (Ber. 23–3075), a few years later went over the same ground with considerable care. They obtained a fairly pure material and determined its pro⁻erties. In the same year Emil Fischer (Ber. 23–3687) published an account of an osazone which he had prepared from grape sugar. This showed about the same properties as the osazone from the gallisin of Scheibler & Mittelmeier. Fischer named his material isomaltose. Subsequent to this considerable work was done, mainly by Lintner and Dull (Ber. 26–2533–28–1523), for the purpose of proving that isomaltose occurred in the products of diastatic fermentation, but this theory was vigorously combatted and final y discredited. The work done at this time by Brown and Morris (Ch. N. 72–45), by Ling and Baker (Ch. N. 71–71), and by Ost (Ch. Z.–19–1504), seemed to prove conclusively that the isomaltose of Lintner and Dull was a mixture of maltose with dextrins. Ost went further than the others and attacked Fischer's isomaltose, but Fischer's vigorous defense as well as the later re-searches of Ost, Ch. Z. 20–762, seemed to prove the existence of isomaltose. The unsatisfactory state of our information upon this subject is well stated by Lippman (Chemie der Zuckerarten-Vol. II, page 1504) in' his excellent bibliography and brief synopsis of the work done along this line, who says that while all investigations known to

him are referred to all, with the exception of Fischer's work on isomaltose, are to be considered as of more or less uncertain value.

For the purpose of studying the unfermentable residue in different hydrolitic products manufactured from starch, the following experiments were made. These are to be regarded as incomplete and the results are published at this time without the attempt to claim or disclaim definitely that gallisin or isomaltose is present in these products, but simply as additional data regarding the composition of starch hydrolitic products.

The aim has been to remove all of the sugars by means of yeast fermentation and then examine the unfermentable residue. Various proportions of sugar, yeast and water were used but the best results were obtained by using a 20% sugar solution, adding 5 grams yeast to 100 cc sugar and allowing fermentation to continue for ten to fourteen days. As a check on complete fermentation under these conditions, a like amount of yeast was added to the unfermented residue after the alcohol had been removed and the material concentrated to about its original density, but there was no evidence of further action.

The unfermented residue was examined both before the removal of the alcohol, and after the alcohol had been driven off and the solution concentrated. The reducing value "K", in terms of dextrose was determined and the specific rotary power for the sodium ray. The value "K" was determined volumetrically by means of a Fehling solution standardized by use of pure dextrose before each experiment. The rotation was observed in a Schmidt-Haensche circular scale instrument after cleaning with alumina cream and without addition of lead acetate. Sodium light was employed. Several kinds of commercial and brewers' yeasts were tried, but the best results were obtained by using a special yeast, which was found to contain no soluble reducing matter or optically active bodies. Fermentation was allowed to proceed at room temperature.

Experiments were made with the following materials:

Expt. 1. Glucose or starch syrup, Be. 43° at 100F, water 17.2%, 10 grams glucose, and 1 gram compressed yeast, taken per 100 cc. water.

Expt. 2. "70" grape sugar, water 16.0%, 10 grams sugar and

1 gram brewers yeast (calc. to dry substance) taken per 100 cc. water.

Expt. 3.   "70" grape sugar, water 17.8%, 20 grams sugar and 2 grams compressed yeast per 100 cc. water.   Fermentation 10 days at 20 to 25° C.   Unfermented residue cleared with alumina cream and filtered.

Expt. 4.   "80" grape sugar, water 12.5%, 20 grams sugar and 2 grams compressed yeast per 100 cc. water.   Fermentation 10 days at 20 to 25°C.   Unfermented residue cleared with alumina cream and filtered.

Expt. 5A.   Special sugar from the impure liquor remaining after removing commercial dextrose.   Water 16.3%.   Solution in water made to 20.5° Brix and ½ grams compressed yeast added per 100 cc.   Fermentation was continued for ten days at 20 to 25°C.

Expt. 5B.   A portion of the unfermented residue was examined after removal of the alcohol and concentration and the results given under Expt. 5B beyond.

Expt. 5C.   The remainder of the unfermented residue was concentrated to 13.2 Brix., cleared with alumina cream and 1 gram yeast per 100 cc. added and allowed to remain 7 days at 20 to 25°C., when it was cleared with alumina cream and filtered.

The following tables epitomize the analytical data for each of the five experiments here summarized.   The figures refer to dry substance in all cases.

Expt.	Dextrose Equivalent K %	Specific Rotary Power Sd	Nitrogen %	Ash %	Material in 100 cc.
1	45.4	112.0	.030	.60	8.38
2	84.3		.031	.70	8.40
3	90.0		.036	.73	16.56
4	89.5		.045	1.37	17.50
5	88.8	67.2	.062	2.20	22.14

The determinations of the dextrose equivalent (K) and the specific rotary power (S_d) in the unfermented residue were made on the unconcentrated material in Experiments 3, 4 and 5A and on the concentrated material in Experiments 1, 2, 5A, 5B and

5C. Concentration was effected on a water bath, under atmospheric pressure. Solids in these residues were determined by mixing with sand drying to constant weight in a vacuum at 90 to 95° C.

The analyses of the unfermented residues in these experiments are summarized in the following table:

Expt.	K %	Sd °	Nitrogen %	Ash %	Solids in 100 cc. grams	In organic matter K %	Sd °
1	22.3	165.7	.048	1.0	5.28	22.5	167.4
2	18.8	31.1	.137	3.2	1.85	19.4	32.1
3	20.7	29.9	1.062	5.1	2.51	21.8	31.5
4	21.6	14.1	1.139	13.0	2.07	24.8	16.2
5-a	25.3	40.0	.336	10.8	4.37	28.3	44.8
5-b	25.4	39.5	.336	10.8	14.21	28.4	44.3
5-c	25.8	40.6	.288	11.3	15.37	29.1	45.8

From the unfermentable residue obtained in Experiment 5C an osazone was prepared according to the method of Fischer (Ber. 23–3687). No precipitate appeared in the hot liquor, indicating that all the dextrose had been fermented. On cooling the solution, a considerable quantity of an osazone separated out and this was recrystallized four times from water. Its crystalline form throughout consisted of aggregates of fine yellow needles. The melting point of the final product was 120°. The crystalline form agrees with that reported by Fischer (Ber. 23–3687) and Ost (Ch. Z. 20. 762). Fischer found the melting point to be 158°; Ost found 140°–155°, Brown and Morris, Ling and Baker and Ost found that a mixture of maltose and dextrin gave an osazone having a melting point much lower than that of pure maltosazone. It seems probable that the low melting point of the osazone prepared in this experiment is due to the presence of impurities not dextrins because of their low rotation values, but more probably some of the caramelization products of the sugars.

While all of the above experiments were made with equal care, Expt. No. 5 must be considered as the most reliable, for several reasons. In the first place completeness of fermentation was assured by further treatment of a portion of the unfermented

residue with fresh yeast. (Expt. 5C). Then, further, there was found no more nitrogenous matter in the residue than could be accounted for by the amount present in the original material, while in Expts. 3 and 4 the large amount of yeast used apparently introduced some soluble nitrogenous matter into the unfermented residue, while in Expts. 1 and 2 no determinations of nitrogen in the residue were made.

It will be observed that seven days further fermentation of the residue in Expt. 5A did not change the character of the residue as is shown in the results in Expt. 5B. It is also very interesting to observe that there was very little difference even in the constants of the dialyzed material. A little nitrogenous matter was removed, a slight excess of ash introduced and the values for K and S_d very slightly increased.

The fact that no precipitate separated from the hot solution proves that no more than minute traces of dextrose remained in the unfermented residue. The melting point of the osazone was so low that no appreciable quantity of maltose could be present. These considerations taken in connection with the low optical activity of the unfermented residue point to the presence of a reducing matter which cannot be accounted for by any mixture of maltose or dextrose with dextrin.

The melting point and crystalline form of the osazone make it appear highly probable that the isomaltose prepared by Fischer occurs in some of the more completely hydrolyzed products of starch, such as grape sugar, and possibly in liquid glucose. But before this point can be definitely established, the nature of the substances which occur with the isomaltose in the unfermentable residue must be determined.

A STUDY OF SOME OF THE PHYSICAL PROPERTIES OF STARCHES

By Hambden Buel
Cliffside, N. J.

In the manufacture of starches to satisfy the various trade industries both the producer and the consumer have long endeavored to evolve some method of testing the starch which would determine at once its suitability for any or some specified use. The consumer usually has but one usage to contend with, while the producer is confronted with almost endless applications.

The methods which are most generally used are those which aim at an expression of the consistency of the starch paste. To arrive at such an expression in known terms which may at the same time be comparable, different experimenters have devised numberless methods with almost as many varying results. These methods may be roughly divided into three general classes, viz., first, those which measure the resistance to the movement of a suspended body in a given paste; second, those which either measure the ability of a given paste to support a known weight on an examination of the body consistency; and third, those which measure the flow of a given paste. While these methods considered individually may show some very interesting results, when compared with one another they will almost invariably show more or less discrepancy. This discrepancy the author believes may generally be traced to an oversight in properly standardizing the instrument used.

A few years ago the author had occasion to investigate some of these various methods with the point in view of fixing upon one which would be accurate and easily manipulated and at the same time be applicable to the various types and grades of starches with consideration for the properties desired in their different applications. The method then in use was a very simple one, but not very carefully worked out, but exceedingly easy of manipulation. It was this latter point that finally fixed its adoption, after the s everal defects had been corrected.
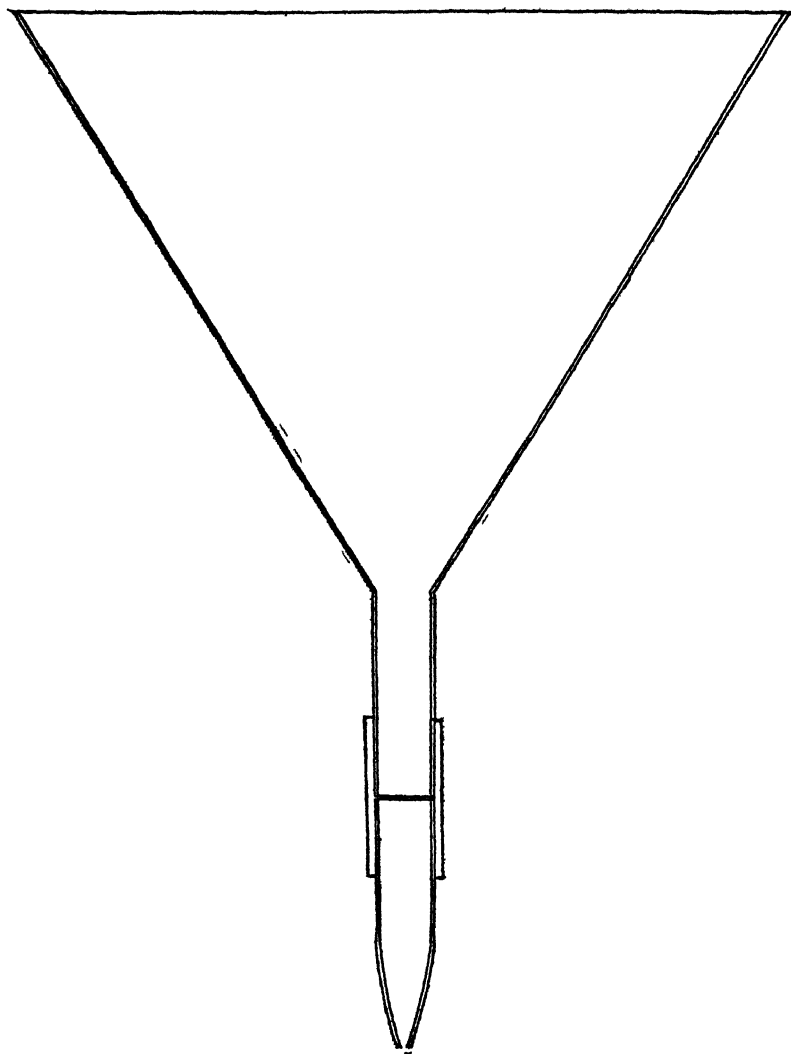
Fig. 1
Scale - 3/4" = 1"

The method in brief is one of the third type heretofore menti med and for convenience in future discussion will be designated as the C. P. R. method.   The instrument consists of a glass funnel with the stem cut off at a given length and a glass tip connected with a piece of rubber tubing, see Fig. 1.   This manner of connecting the tip was to facilitate the cleaning when used for a heavy paste. No provision for temperature control in the instrument itself has been made as the paste is tested as soon as transferred, the funnel having just previously been rinsed in water of the desired tempera-ture.   The instruments are first regulated so that they will deliver 105 cc. of water in 70 seconds starting with 125 cc. at 25 degrees C. This determination of the water value is only a preliminary step, the actual standardization being carried out by the use of starches giving pastes of varying consistencies, which consistency has been accurately determined with a funnel and tip which is preserved as a "master instrument" and by which all other instruments are controlled.

The method used is as follows: Five grammes of starch is weighed into a 250 cc. beaker and brought into suspension with 10 cc. of water, then 90 cc. of a 1% sodium hydroxide solution of 25 degrees C. is added and the whole stirred for three minutes at the rate of 70 to 80 R.P.M.   The beaker is then placed in a water bath for thirty minutes in which a constant temperature of 25 degrees C. is maintained.   About twenty seconds before the ex-piration of the full thirty minutes the beaker is removed and the starch paste is poured into the instrument and a 100 cc. graduated cylinder is brought under the delivery point by a very short and quick movement at the expiration of the thirty minutes.   At the end of seventy seconds the graduated cylinder is removed and the reading in cc. represent the observed fluidity.   This observed fluidity is then corrected by means of a curve which is made out for each instrument.   A stop-watch is always used in connection with these determinations.

The sodium hydroxiate method is employed because it may be more accurately controlled at the critical points than can the aque-ous paste method, and the temperature of 25 degrees C. is used because it is nearer a mean temperature for a laboratory, year in and year out.

In order to insure the greatest accuracy in the method it was necessary to determine the essential controlling factors, which were found to be as follows:

First: the strength of the sodium hydroxide solution used.

	%	%	%	%	%	%
Strength of NaOH sol.	.5	.8	.9	1.	2.	3.
Weight of starch — gr.	5.	5.	5.	5.	5.	5.
CC. of water used	10.	10.	10.	10.	10.	10.
CC. of NaOH sol. used	90.	90.	90.	90.	90.	90.
Fluidity as determined	Would not gelatanize	Partially gelatanized	34.1	34.0	53.5	54.2

Second: The effect of variations in temperature. In this as well as in the remaining tests the quantities of starch, water and NaOH sol. was the same as called for in the description of the method, the same starch being used throughout.

Temperature	Fluidity
15.° C.	23.9
25.° C.	34.0
35.° C.	45.2

Third: The time the mixture should be allowed to stand.

After standing 15 minutes	29.4 Fluidity
After standing 30 minutes	34.1 Fluidity
After standing 45 minutes	35.7 Fluidity

Fourth: The effect of the rate of stirring.

R. P. M	Fluidity
75	34.0
150	37.8

As the foregoing experiments covered all of the manipulations under which the test is made it was decided to use the constants as given in an earlier paragraph describing the method. These constants, as will readily be seen, may all be controlled with great accuracy and with a minimum of effort.

Having disposed of the question of the controlling factors the next points that came up were the comparative results of different instruments and of different operators. It was very soon found to be practically impossible to construct different instruments that would give identical results, so it was decided to standardize all future instruments according to one preserved as a " master

instrument." This solution of the problem turned out to be very satisfactory as may be seen from the results given in Table 1. This table shows both the comparative results of different operators and different instruments.

TABLE 1

Operator Instrument	Corrected Fluidity		
	A 23	B 23	C 12
Starch No. 1 (ordinary)	1.7		2.2
Starch No. 2 (modified)	17.3	17.7	17.6
Starch No. 3 (modified)	33.5	33.1	31.0
Starch No. 4 (modified)	39.6	39.7	39.2
Starch No. 5 (modified)	48.5	48.8	49.3
Starch No. 6 (modified)	62.6	61.8	60.3
Starch No. 7 (modified)	74.5	73.2	75.5
Starch No. 8 (modified)	81.0		82.4
Starch No. 9 (modified)	90.0		90.1
Starch No. 10 (modified)	20.9	21.0	21.1
Starch No. 11 (modified)	39.5	40.0	40.1
Starch No. 12 (modified)	50.0	49.5	50.0
Starch No. 13 (modified)	62.6	62.0	62.3

This table shows very liberally the range of variations of different operators using different instruments. As the full investigation embraces the work on upward of forty instruments and nearly twenty operators, most of whom were connected with different and independent laboratories, a tabulation of the complete results would entail too much space for the purposes of this paper.

TABLE 2

Showing the standardization of the instruments.

Instrument Operator	Observed Fluidity						
	No. 32		No. 33		No. 34		Master
	A	B	A	B	A	B	Inst.
Starch No. 1 (ordinary)	2.1	2.2	2.1	1.9	3.4	3.3	1.6
Starch No. 2 (modified)	20.2	20.5	19.0	19.5	25.2	25.0	16.9
Starch No. 3 (modified)	35.3	36.3	33.5	36.0	46.9	46.7	30.1
Starch No. 4 (modified)	44.4	45.0	41.7	42.5	57.0	57.8	37.3
Starch No. 5 (modified)	54.2	54.3	52.0	52.7	68.2	68.4	46.5
Starch No. 6 (modified)	67.0	67.0	65.2	65.0	80.3	79.5	60.6
Starch No. 7 (modified)	82.9	83.7	81.1	81.2	91.0	91.0	78.7
Starch No. 8 (modified)	86.9	86.8	85.5	85.2	93.2	93.3	82.9
Starch No. 9 (modified)	92.3	94.0	90.8	91.8	96.1	95.6	89.7

The correction curve is then plotted from the figures thus obtained in Table 2. The fluidity as shown by the "master instrument" is taken as the standard and the average results of the two operators on each instrument are taken from the points of the curve for that instrument. The correction curves for the above three instruments are shown in Figure 2.

The next matter to come up for consideration was the comparative results with different types of instruments.

The first one was that used by a large starch consumer. This instrument was in the shape of a long cylinder about one inch in diameter and fifteen inches long, the lower end of which was drawn out to a small orifice and having zero and 100 cc. marks about nine inches and three inches from the bottom respectively. A glass rod with a ground seat extending down on the inside of the tube was used to start and stop the flow. The sodium hydroxide paste is used and the results show the time required for the delivery of 100 cc., which is the reverse of the results by the C.P.R. method.

These instruments were only standardized to a water value and the error in not further and more thoroughly standardizing them may be seen from the results shown in Table 3.

TABLE 3

Instrument	Blank	Viscosity No. 3	No. 6
Water	38 3/5 sec.	38 2/5 sec.	38 2/5 sec.
Starch No. 1, C.P.R. fluidity 51.0	60 2/5 sec.	74 1/5 sec.	49 sec.
Starch No. 2, C.P.R. fluidity 21.0	101 2/5 sec.	144 1/5 sec.	74 4/5 sec.
Starch No. 3, C.P.R. fluidity 49.0	63 2/5 sec.	77 4/5 sec.	50 sec.

Subsequent work with these instruments embracing upward of 200 determinations showed that after the starch value had been properly determined the results were quite consistent.

The next instrument taken up was the Doolittle Tortion Viscosimeter. This method makes use of an aqueous paste and the comparative results may be seen in Table 4. The values of this instrument are the reverse of those indicated by the C.P.R. method.
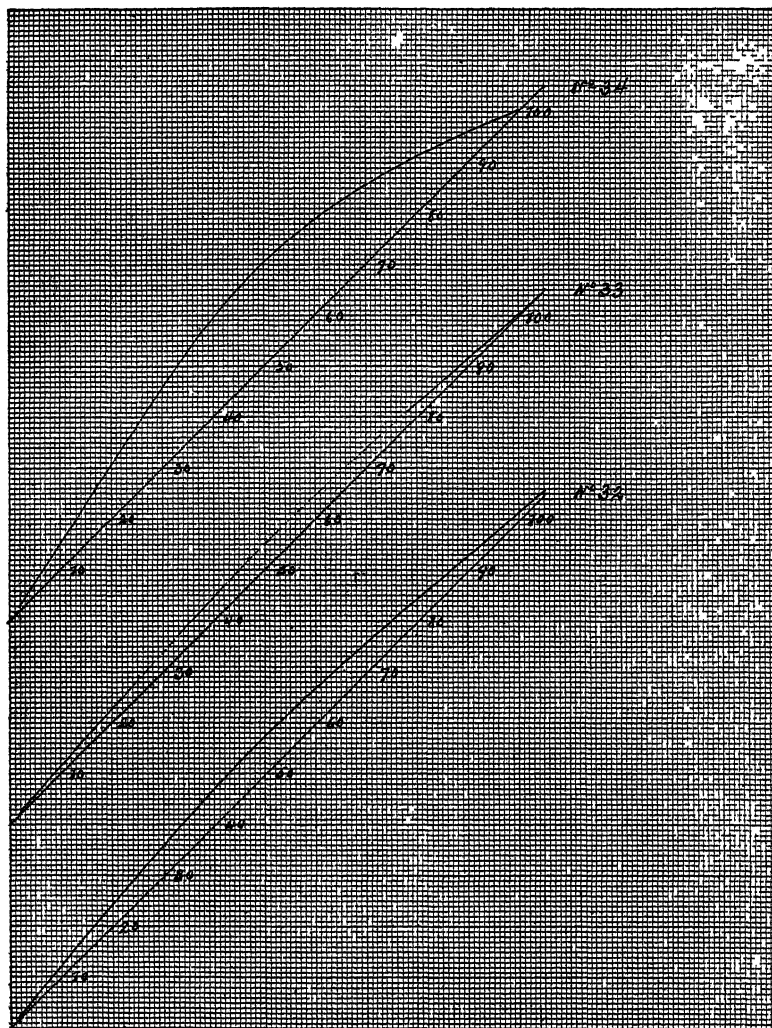
Fig. 2.

TABLE 4

	C. P. R. Fluidity	Doolittle Viscosity
		Too thick to test
Starch No. 192	13.0	
Starch No. 194	18.5	100.
Starch No. 195	20.6	99.
Starch No. 193	21.2	98.4
Starch No. 198	36.8	84.9
Starch No. 191	48.6	75.8
Starch No. 199	54.5	74.5
Starch No. 203	57.5	70.7
Starch No. 204	58.1	71.5
Starch No. 200	67.1	64.7

The Doolittle Viscosimeter is a very well constructed and standardized instrument. However, when it is employed for the determination of viscosities in starch pastes it cannot be used without varying the strength of the pastes for widely different starches. For instance, the quantity of the soluble or highly modified starch that would be required to give a paste of the proper consistency for using with the instrument would give an entirely too stiff a paste with a thick boiling starch. In an effort to overcome this objection experiments were made with wires of different sizes, but without any very satisfactory results. As to the manipulations, these were not nearly so simple or easily controlled as in the C.P.R. method. One very serious objection was the corrosion of the delicate wire. Although the instrument was kept in a special glass case, it was found that the wire would slowly become weaker, which fact would necessitate a restandardization from time to time.

Three other methods were also tried, viz.: first, the Rustless Nickel Steel Viscosimeter; second, one proposing to determine the ability of a given paste to support a known weight; and third, a method proposed by Dr. Th. Breyer of Chicago.

The first of these methods consists of a copper water jacket about nine inches in diameter and five inches deep, in which is fixed a heavy nickel-steel cup holding about 300 cc. with a small orifice tube about one inch long screwed in at the bottom and projecting upon the inside of the cup about half an inch. These orifice tubes may be procured in different sizes. Either the sodium
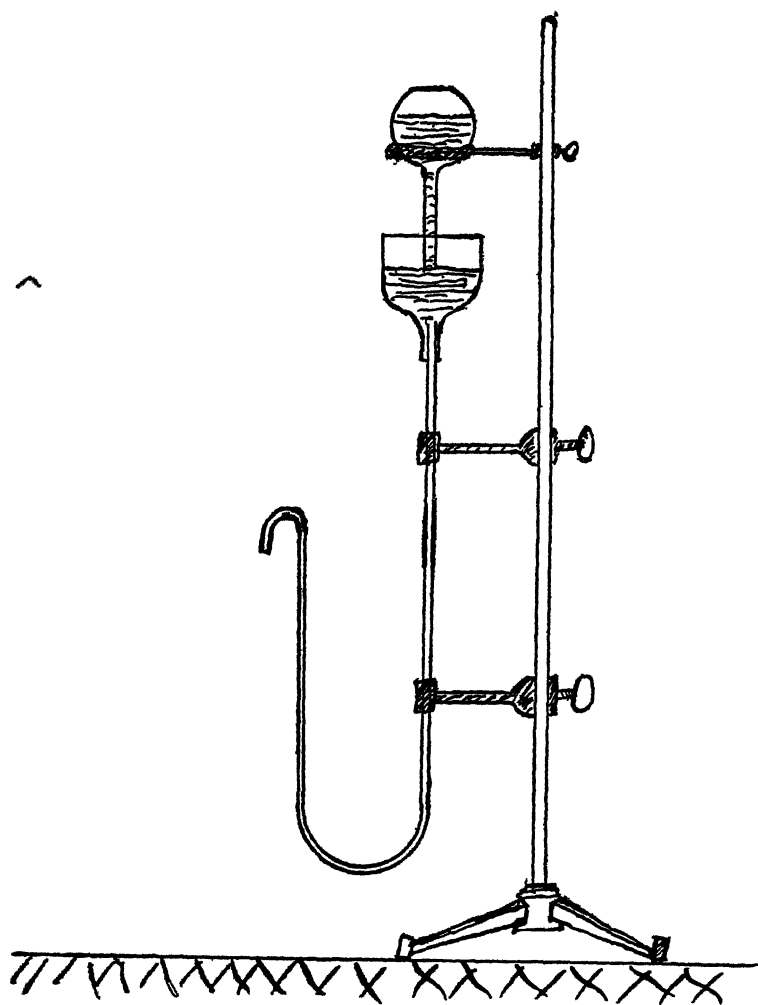
Fig. 3   *Scale 1″= 5″*

hydroxide or aqueous paste may be used with the instrument, but it was found that the orifice tubes of supposedly the same size did not give corresponding results and would therefore have to be standardized as in the C.P.R. method. Furthermore, it was not so easy to handle as the latter.

In the second method there were found to be two chief objections. First, the great difficulty of controlling the important factors in preparing the paste. Second, in working with starches of widely different characters it necessitated a preliminary test in order to determine approximately the quantity of starch to be used to give a paste of the desired consistency.

The method proposed by Dr. Breyer is extremely unique and possesses one important advantage in that it provides for a constant head. See Figure 3. The main part of this instrument, the long bent glass tube, is made from barometer tubing of specified diameter. The construction of the instrument in its main features is rather delicate and is hardly capable of being quickly cleaned. Furthermore, because of the great length of the small 'glass tube, which is essential since it depends upon the skin friction of a thin solution, should be provided with a constant temperature jacket, because the time required for the solution to traverse the full length, in conjunction with the small volume, makes it very susceptible to slightly varying changes in temperature. This instrument will permit of the use of either the sodium hydroxide or aqueous pastes and when corrected for the above-mentioned defects and properly standardized might prove to be exceedingly valuable.

In conjunction with the regular tests by the C.P.R. method there has been carried on a very simple check test. This "check test" consists of simply boiling a given weight of starch in a given amount of water for a fixed time and transferring same to a funnel with a tuft of cotton in the apex and covering the funnel with a piece of paper, and setting aside over night at room temperature. The following morning the starch jelly is shaken out from the funnel and its consistency examined by hand and the comparative results noted along side that of the determined fluidity. These comparative results have embraced all types and grades of starches and cover upward of two thousand determinations.

The results of these comparative tests mentioned in the foregoing paragraph have shown the determinations as made by the C.P.R. method to be highly consistent. It should be noted here that it is not the intention to critically compare the consistency of one type of starch with that of another except in a general way. Extensive investigations have shown that the different types such as corn, cassava, potato, rice, wheat, etc., each have their own distinctive characteristics. Starches of different types, but of the same fluidity, usually produce pastes of widely different characters, *i.e.*, a wheat would give a paste of a mush-like consistency, while potato would give a paste more gum-like, whereas that of corn would be between the two. Furthermore these characteristics might be varied to a certain extent by the manner of preparation, such as in the time of cooking, stirring, standing, etc.

In an earlier part of this paper it was stated that the C.P.R. instrument was first regulated to a specified water delivery using 125 cc. of water, while the actual fluidity determinations are carried out with 100 cc. of solution plus the weight of the starch used. It will, of course, be seen that the head will be variable with the different fluidity starches. This latter point, which in itself would be serious, becomes practically negligible when it is considered that each instrument is standardized against a "master instrument" for different fluidity starches and the corresponding correction curve will reduce all results to a common basis. The actual use of these instruments in regular daily control work in producing uniform starches constitutes after all their highest endorsement.

Further experiments along different lines showed numerous inherent peculiarities, chief of which may be mentioned in brief, as follows:

First: It was observed that modified starches of an acid character usually showed an increasing fluidity with age varying from 4 to 10 points in the lapse of five months.

Second: The aqueous paste tests were shown to be susceptible to variations in the time of cooking as follows:

Time cooked	Fluidity
3 minutes	42.5
4 minutes	15.0
5 minutes	7.5
7 minutes	4.0
10 minutes	3.0

This was also a variable quantity with the different types of starches.

Third: The aqueous paste tests when prepared and cooked in the same way showed varying fluidities when allowed to stand different lengths of time, to wit:

Time cooked	Time cooled	Fluidity
3 minutes	1 hour	23.0
3 minutes	2 hours	16.5
3 minutes	3 hours	4.5
3 minutes	6 hours	.2
5 minutes	½ hour	10.0
5 minutes	1 hour	4.0
5 minutes	4 hours	6 drops

Fourth: A large sample of starch was divided into nine parts and dried at low temperature to different moisture content and the fluidities determined with the following results:

Moisture	Fluidity
16.66 original sample	72.7
13.51	70.7
12.76	69.8
12.07	69.6
11.10	69.3
10.30	69.0
6.90	67.3
4.00	66.2
.30	63.4

This experiment in reality shows the relationship of fluidity to dry substance.

Fifth: Different types and grades of dry starches were exposed under varying conditions of time and humidity, but no especially interesting results were obtained, though some starches did differ from others as to the amount of moisture they would take up.

! There are severa agents when present in a starch influences its character to a greater or less degree. Acids will cause a lique-faction in the starch paste, while alkalis and borax will usually

produce a stiffening effect when present in a certain amount. Lastly a starch may have become contaminated with micro-organisms at some point or other of its manufacture or handling, and contain very resistent spores of a form that develops diastatic enzymes. Such forms, of course, will have a liquifying action upon a starch paste, which action may not become apparent until after the starch has stood several hours.

In the general question of paste consistency there are two points that it might be well to bear in mind; first, whether it would be best that the method should be applicable to all starches for a given purpose; or second, whether it should be applicable to all starches irrespective of any particular use. In other words, should it have a narrow or broad application?

If it were possible to devise a method for the narrower application, as for instance the determination of the suitability of any particular starch for laundry purposes it would be very well, but this is hardly apt to be realized. There are too many individual characteristics in starches that act differently under the various conditions. Not long since one very large user of laundry starch, who was using a Doolittle instrument with considerable satisfaction, was confronted with a starch which his test would have condemned, but subsequent use in the laundry proved it to be highly satisfactory.

The real value of a consistency test might prove of greater worth if it were perfected in line with the broader application. Worked out along this line it should be regarded with due consideration of the individual characteristics of the particular starch to be tested, its intended use, and the conditions affecting its use. For instance, a laundry has been using a wheat starch for certain purposes having a fluidity of say 50. As long as it uses this particular type of starch the simple consistency test may be sufficient to determine its value. But suppose that the laundry be given a corn or potato starch of the same fluidity, it would probably be found that the standard used for wheat would be incorrect if applied to the corn or potato starch, although other grades of these two latter starches might give equal satisfaction.

An additional property of starches and one not heretofore emphasized, but which may be found to play a very important

part in their application to various usages, is that of cohesion. A close study of this propeity may reveal some very interesting facts.

In connection with some of the work herein cited the author wishes to acknowledge his indebtedness to H. C. Humphrey and Chr. E. G. Porst for several valuable suggestions.

SCIENTIFIC CONTROL OF SULPHITE PULP MANUFACTURE

By Charles M. Bullard
Boston, Mass.

In the year 1884, at Rumford, R. I., the first sulphite mill in America was built and operated by the Richmond Paper Company. Since that time there have been built 102 sulphite mills in America of approximately 5200 tons daily capacity in bleached and unbleached sulphite fibre.

To produce this enormous amount of fibre, it is safe to say that approximately 12,000 cords of wood, 1,500,000 lbs. of sulphur and 1,200,000 lbs. of lime and its equivalent in limestone is used per 24 hours, or an average of $2\frac{1}{4}$ cords of unpeeled wood, 280 lbs. of sulphur, and 235 lbs. of lime per ton of product.

In discussing the various phases of sulphite manufacture, this paper will deal with the unbleached product on'y, and to determine the amounts of raw materials used on a bleached basis it is safe to add 10% to any figures given.

The most expensive raw material entering into the manufacture of sulphite pulp is wood. Its price varies greatly in different localities and under varying conditions and is steadily advancing from year to year. It is safe to say, however, that it will not average less than $8.00 per cord, and that an average of $2\frac{1}{4}$ cords is used per ton of sulphite produced. Figuring on this basis the total amount of wood used is costing the mills approximately $96,000 per 24 hours or $18.00 per ton of product.

The next expensive raw material is sulphur. Its price varies but slightly for different localities and averages $23.00 per ton, therefore the mills will spend about $18,000 per 24 hours for this material, or on a tonnage basis their sulphur is costing them $3.64 per ton of sulphite.

Lime is the cheapest material used and its average co t is 30c. per hundred. The average amount used is 235 lbs. per ton,

therefore this material is costing the mills $3600 per 24 hours or about 71c. per ton of product.

The users of sulphite today are demanding more and more as regards strength, color and cleanliness, and to meet this demand and still make a fair margin oᶠ profit the manufacturers must necessarily reduce the cost of production in every possible way, as their profit does not so much depend on the market price, which is fairly stable, as on the cost of production.

The manufacturers do not appreciate the countless ways where scientific control of every stage of the sulphite process will surely aid them to reduce this cost, and still maintain or improve the quality of production, and the sooner they realize that the old ''rule of thumb method'' so much in vogue in the past should be supplemented by the latest and most improved methods, the sooner they will be enabled to pay greater dividends and still compete with European manufacturers, where the cost of labor and raw material is much lower than in America, and especially in the United States.

The lack of scientific control and failure to make use of scientific methods in the average mill is the direct cause for the needless expenditure of large sums of money during the process, for such results as they are getting, both as to cost of production and quality of product, and were they to skillfully compare their operations in every stage of the process and the results therefrom with those of the few who have applied scientific methods and given them a fair trial, they would at once appreciate the value of these methods.

A very few have made use of these methods and control in their lumbering operations and by so doing have demonstrated its value. In the majority of cases, however, these operations are costing the manufacturers or operators excessively in labor, but what is of equal or more importance is the question of wood waste.

The writer has seen many instances where this waste was enormous. Large quantities of available and valuable wood in the form of tops and large limbs are left scattered broadcast, which are a menace to standing timber from fire. Another large loss is due to not cutting close enough to the ground and many tons are unskillfully felled in inaccessable places where they are

left to decay. These losses are mainly due to the lack of appreciation of what could be saved were these operations scientifically controlled.

In the handling, storage, and delivery of wood to and through the wood room, it is remarkable what can be done in many mills by carefully studying their individual needs and conditions. In one instance out of many, the wood room cost $1.37 per ton. Their needs and conditions were carefully studied and various changes made in apparatus and methods, with the result that more wood is being handled with less labor and waste, at a cost of 61c. per ton, and there is still room for improvement.

A good deal of argument has come up from time to time as to which was the more economical method for barking wood, to peel it in the woods during the peeling season or at the mill by the usual mechanical method. It would seem that the former method was to be generally favored as the loss is about 9% as against an average of 25% by mechanical barking, and in many instances will run much higher.

The former method will certainly allow much more thorough and uniform drying or seasoning, which is highly important, and when the wood is delivered to the mills by rail and the freight charged by weight as is usual, we should expect a very large saving in the first cost of wood.

Wherever wood is being barked at the mill by the usual mechanical method (by the use of the ordinary disc barker) the use of scientific methods will show very large savings in wood wastes and increased capacity of wood room. Many careful tests made by weight have shown the loss during this operation to run as high as 30%, when under proper conditions this should not run over 21%, and in some instances even less. Such conditions actually exist, and the savings which it is possible to make are therefore very apparent.

A very recent instance of what can be done in this direction will serve to illustrate the value of proper control of the barking operations. A mill was barking approximately 200 cords of wood per day. Careful tests made by weight showed a loss of $28\frac{1}{2}$% during this operation. Various inexpensive changes were made, principally by changing the speed at which the stick was turned while in contact with the barker disc, increasing the speed of the

disc, decreasing the set of the barker knives, and then tests made showed the loss to be reduced to 22%, or a saving of 6½%, equivalent to 13 cords saved per 24 hours.

The yield per cord and quality of fibre is very largely controlled by the uniformity of chips produced, and this uniformity, as well as the amount of sawdust and sulphite screenings (which are a direct loss) are directly controlled by the condit ons of the chipper, its speed and the manner of supplying the wood to it. The average amount of sawdust, which is a clear loss, is not less than 5% of all wood chipped, while the sulphite screenings will not average less than 5%. In the majority of cases these two losses can be reduced 40% by scientifically controlling the chipping operation, which when done represents an enormous saving to the manufacturers.

Very recently a mill was chipping wood for 50 tons production. Careful and exhaustive tests were made to determine the uniformity of chips produced, and the amount of sawdust made. The amount of sawdust was found to be averaging between 6 and 7% and a slightly larger amount·of course chips, slivers and large pieces of uncut wood were formed, which on entering the digesters with the good chips were scarcely if any affected by the acid during the cooking operation, and eventually were lost as screenings.

Careful attention was given to the condition of the chipper as regards grinding and setting of the cutting knives, face plates and bed knife. The speed was then changed and the men attending the chipper instructed as to the best method of delivering the wood to it. After these changes were made, other careful tests showed the loss in sawdust to be reduced 51% and the large chips and uncut wood, which eventually turned up as screenings, were reduced 46%. This represents a very large saving in wood and increased yield per cord.

The acid plant is the heart and nerve center of a su'phite mill, and is usually the most neglected department. At no stage of the whole sulphite process will scientific methods and control show greater return than here.

Many manufacturers seem to think that any one who can shovel sulphur into a burner at his own discretion is fully capable

of handling this very important operation economically and efficiently. They apparently do not appreciate the superiority of one type of burner over another, the requisite amount of burning area which should be available for the greatest economy, the most efficient draft to carry on them under varying conditions, and the best method for supplying or feeding sulphur to them. Many, and I may say the majority, do not seem to realize that without proper air and temperate control in the burners, from 5 to 10% of sulphur burned may be oxidized to SO_3 (nor make any attempt to determine this), which in itself is a direct loss, but later in the operation will cause still more loss in lime from the formation of calcium sulphate. This in turn causes another loss in labor, production and innumerable troubles by the plugging up of pipes, bottoms of digesters and blow-pits, and eventually shows up in the finished product.

The strength and purity of gas produced on entering the acid systems is not given the attention which it demands for the best results and the majority of mills do not even make analysis to determine this. If every manufacturer realized the importance of eliminating every air leak throughout the entire acid making system, properly controlled the temperatures during the various stages of the process, doubled and in many instances trebled the lime slacking capacity, properly introduced and distributed the digester relief in the acid storage and reclaiming tanks, with proper temperature control, they would be astonished at the great improvements in efficiency and economy during the acid making process, as well as the decrease in the consumption of sulphur and lime per thousand gallons of acid made.

It is remarkable how little it takes to demoralize the acid making process which will cause the cost to go up with leaps and bounds, and still how simple and economical this process can be handled by applying scientific methods.

The cooking of wood requires the most careful and uniform control if the best results as regards maximum yield, strength and color are obtained. These results are directly controlled by pressures and temperatures carried in the digesters and manner of relief during this operation, and were the manufacturers to realize this and carry on this cooking operation on a scientific basis, very greatly improved results would be obtained.

Many do not seem to appreciate the ill effects of high temperatures, especially during the first part of the cook, and this being controlled by the relief, directly influences the retention of acid strength during the cook so necessary for the best results.

It is quite impossible to make any set rule as to the exact manner in which every digester should be handled, as conditions vary so widely in different mills, and it is therefore necessary to scientifically study their conditions and needs in order to determine what method should be followed to produce the best results. When this is done, and these methods enforced, the desired results are sure to follow.

In many mills the great variations in quality is the cause for wonder, worry and poor results. On the other hand it is possible to remove or prevent the troubles due to this variation by applying and adhering to improved methods during the cooking process, as there is always a reason for every result obtained whether it be good or poor. The washing, handling and scouring of sulphite is usually considered a purely mechanical proposition and in a large measure this is true, but even here the scientific study of conditions and needs and application of improved methods will almost invariably demonstrate their value in the savings in power, labor and increased efficiency, and its general adoption will be the means, and I may say is the only means of successfully solving the many perplexing problems which are constantly coming up during the whole process of the manufacture of sulphite pulp.
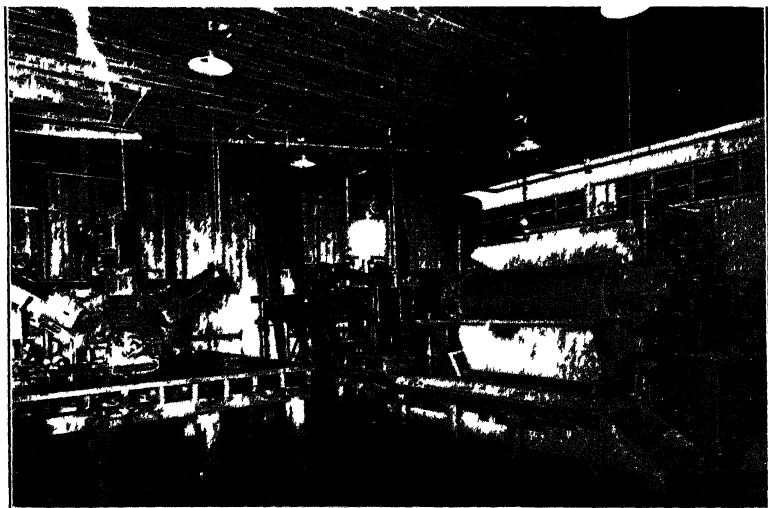
PLATE 1
Figure 1   VIEW OF GRINDER ROOM
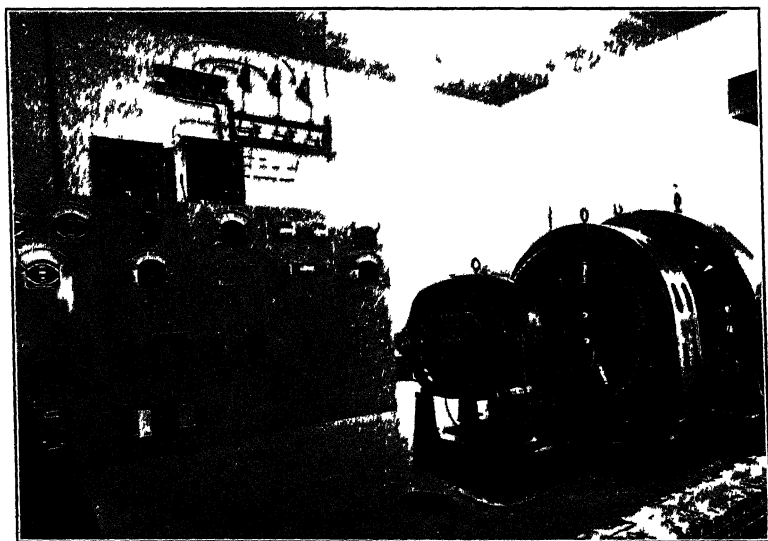
PLATE 1
Figure 2.   A PORTION OF THE ELECTRICAL EQUIPMENT

THE EFFECT OF VARIABLE GRINDING CONDITIONS ON THE QUALITY AND PRODUCTION OF MECHANICAL PULP

By McGarney Cline and J. H. Thickens
Madison, Wisconsin

INTRODUCTION

Briefly stated, mechanical pulp is produced by pressing sections of log against a revolving grindstone, which may or may not be revolving in a pit of moist pulp. If revolving in thick pulp the hot grinding process is employed; if a large excess of water is used the resultant process is one of cold grinding. The factors which enter into the production of mechanical pulp from any species of wood are:

1. The surface of stone; whether rough or smooth, sharp or dull, or of coarse or fine grit.
2. The pressure with which the wood is forced upon the stone.
3. The peripheral speed of the stone.
4. The temperature of grinding.
5. The moisture content, weight per cubic foot, and the condition of the wood to be ground.

As a result of operating under different combinations of these factors (different combinations of surface, pressure, speed, temperature, etc.) certain other resultant factors are developed. These are:

1. The horsepower which must be applied to the grinder.
2. The amount of pulp produced in 24 hours (tons of 2000 pounds).
3. The horsepower consumption per ton of pulp in 24 hours.
4. The yield of pulp and screenings per cord of wood ground.
5. The quality of the pulp.

In commercial practice there is wide variation in the method of producing ground-wood pulp. Its manufacture is generally conducted according to certain rules-of-thumb which have been

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developed as a result of long practice. Peculiarly, however, one will hardly find two mills which operate under exactly the same conditions. Each superintendent or manager has his own theories, and, as a result, there are almost as many different methods employed in the manufacture of ground-wood pulp as there are mills. The results obtained from a large number of commercial plants in the United States indicate that the pressure used in grinding varies from 17 pounds per square inch on a 14-inch cylinder to 116 pounds; the peripheral speed from 1360 feet per minute to 4310 feet; the temperature from cold to 153° F., the horsepower connected to a single grinder varies from 135 horsepower in one mill to 625 in another. Likewise the consumption of power per ton of pulp in 24 hours is claimed in one mill as low as 31 horsepower, while in another as high as 125. It is only reasonable to suppose that there is some combination of pressure, speed, power to the grinder, etc., which will give the most efficient and economical results. The experiments upon which this paper is based were carried on for the purpose of determining as accurately as possible the laws underlying the production of mechanical pulp.

<div align="center">EQUIPMENT AND METHODS</div>

The equipment used consisted of a swing cut-off saw, a mechanical barker, a commercial-sized 3-pocket grinder taking a stone 54 inches in diameter by 27 inch face, together with the necessary auxiliary pumps, screens, and a wet machine for the removal of water from the pulp. In screening the pulp a centrifugal screen taking a plate perforated with .065 inch holes was used. The screenings from this machine were rescreened in a flat plate screen, the slots of which are .012 inch wide.

The wood grinder was direct connected to a variable speed, direct current motor, the efficiency of which was known for all speeds and loads, thus making possible the exact determination of power applied to the grinder. Calibrated instruments were used in power measurements and graphic records were taken of the power applied to the grinder and of the temperature of grinding.

In the treatment of woods prior to grinding, a steaming tank 3 feet in diameter by 8 feet high was employed. This tank was
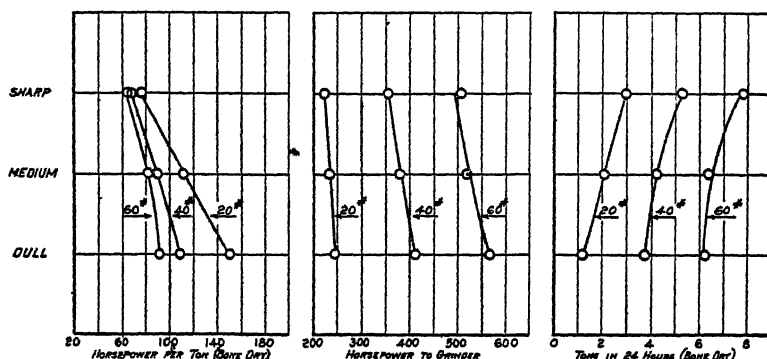
PLATE 2

Condition of Tests.
  Speed: 225 R. P. M.
  Surface: Sharp.   6 to the inch spiral cut (deep grooves).
            Medium.   8 to the inch diamond cut (medium depth).
            Dull.   3 to the inch straight cut and 12 to the inch spiral cut
                     (shallow grooves).
  Process: Hot Grinding.
  Pockets used: 3 at a time.

provided with steam vacuum and water connections. Views of
a portion of the electrical machinery and the grinder room are
given on Plate 1.

  The general method of conducting tests was as follows:

  The desired surface was placed on the pulpstone by means of
a bush roll or burr; and, after measuring the diameter of the stone,
an impression was taken of its surface by means of a piece of
coated paper and a sheet of carbon paper, this record being later
photographed. The wood for the test was sawed into 2-foot lengths,
and the bark removed, sections of the wood being taken for the
determination of moisture content and bone-dry weight per cubic
foot. The stone was cold at the beginning of each test, and the
run was continued until approximately 750 pounds of bone-dry
wood had been ground. The pulp and screenings obtained were
weighed and the moisture content of each determined. During
any test the pressure and speed were maintained as nearly con-
stant as possible. The quality of the pulp was recorded by means
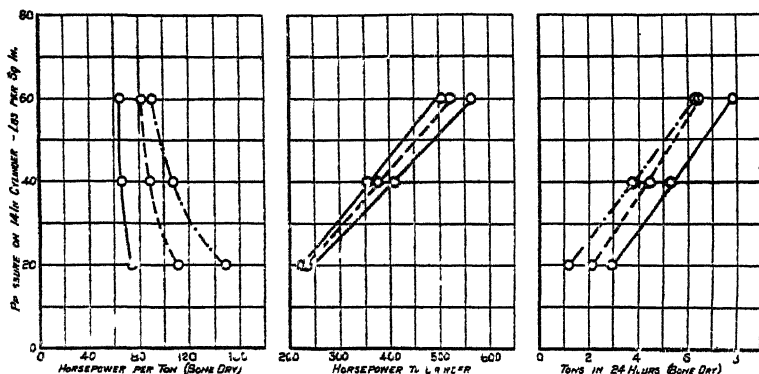
PLATE 4

Conditions of Tests.

   Speed: 225 R. P. M.
   Surface: Full line.   6 to the inch spiral cut.
            Dashed line.   S to the inch diamond cut.
            Dash and dot.   3 to the inch straight cut and 12 to the inch spiral.
   Process: Hot Grinding.
   Pockets used: 3 at a time.

of photomicrographs of the fiber and by manufacturing it into newsprint paper. The samples used in the paper tests were beaten with 20 per cent of bleached spruce sulphite for a period of one hour, then run into a sheet on a 12-inch paper machine. No color, size, alum, or loading was used in making the paper. Tests for color, bursting strength, tensile strength, stretch, etc., were made on the paper samples. This portion of the work has not been completed, however, and the results given are only such as could be deduced from a comparatively small number of tests.

The steaming of wood for tests was carried on for different lengths of time and at different pressures, the condensation being drawn off at frequent intervals. In each case the wood was ground immediately after it was removed from the steamer.

RESULTS

In analyzing the results of the tests a number of relations have been found to exist, and while some of these do not appear in accordance with the results obtained by other investigators, they
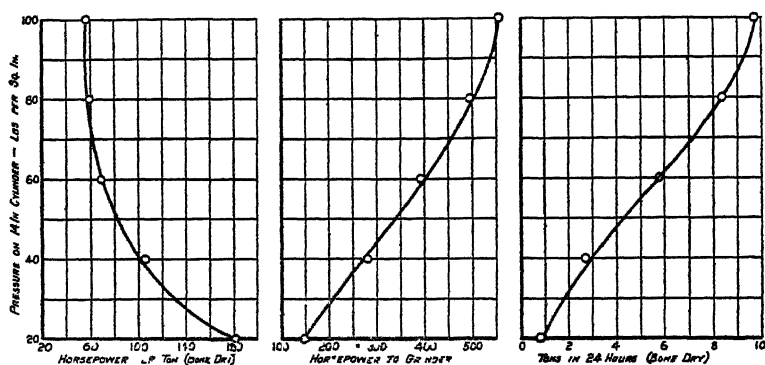
Conditions of Tests.
   Speed: 225 R. P. M.
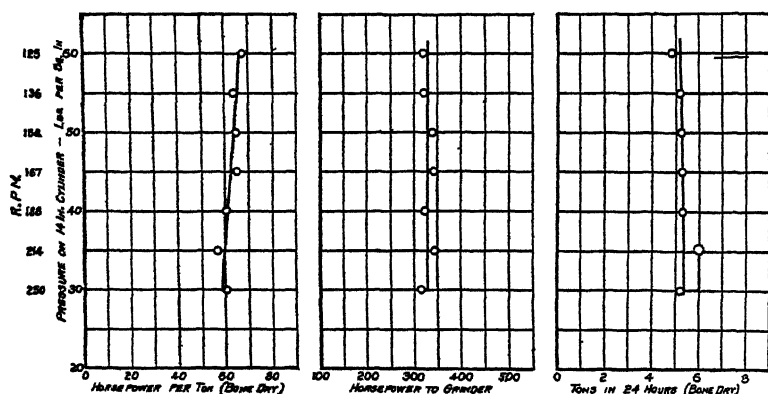   Surface: 3 to the inch straight cut and 12 to the inch spiral.
   Pockets used: 2 at a time.
   Process: Hot Grinding.

have been tried out commercially and found to be essentially
correct.

SURFACE OF STONE

The "surface of stone" involves several different factors; the
size of the sand particles might be the important factor in some
cases, the sharpness of grit the important one in others.   However,
in this series of tests, variations in the surface of the stone were
obtained by working the surface of the same stone with steel
rolls of different design, thus forming upon the stone depressions
of different depths and patterns.

Horsepower per ton.   Horsepower to the grinder.
Production in 24 hours.

Plate 2 shows graphically the relation between the different
surfaces of stone and the horsepower consumption per ton, power
to the grinder, and production in 24 hours.   The curves shown
were obtained at pressures of 20, 40, and 60 pounds.   It will
be noted that the horsepower per ton varies inversely with the
degree of sharpness of the stone.   The horsepower to the grinder
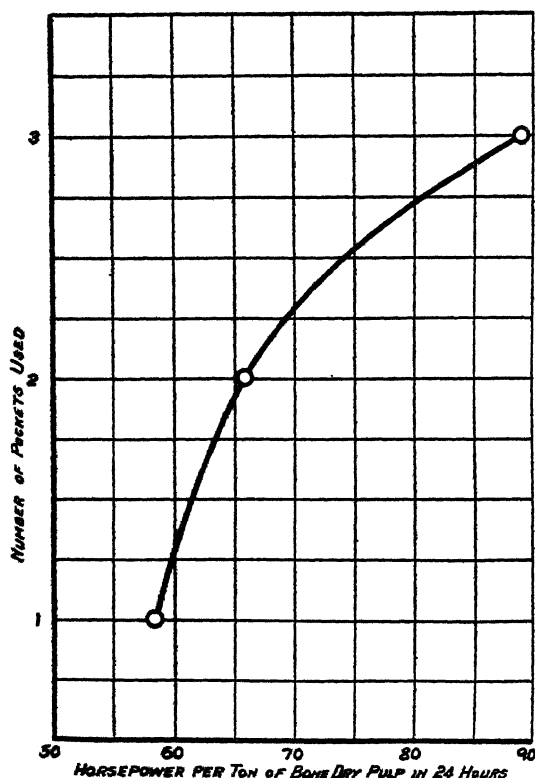
Conditions of Tests.
  Speed: 225 R. P. M.
  Pressures: One Pocket—120 pounds on 14-inch cylinder.
              Two Pockets—59.5 pounds on 14-inch cylinder.
              Three Pockets— 36.5 pounds on 14-inch cylinder.
  Surface: 3 to the inch straight cut and 12 to the inch spiral.
  Power to the Grinder: 330 horsepower.
  Process: Hot Grinding.

varies in like manner, while the production in 24 hours varies
directly with the degree of sharpness.

  One thing which is of particular interest is the fact that the
curves apparently come together at a point corresponding to
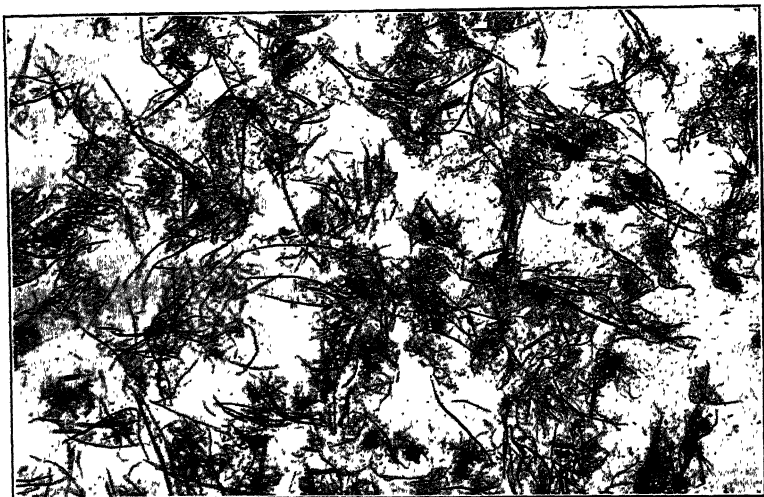
PLATE 3.   Figure 1
PHOTOMICROGRAPH SHOWING THE FIBERS OBTAINED ON DULL STONE
Power Consumption: 84½ horsepower per ton.
Magnification: 15 diameters.

PLATE 3.   Figure 2
PHOTOMICROGRAPH SHOWING THE FIBERS OBTAINED ON SHARP STONE
Power Consumption: 64 horsepower per ton.
Magnification: 15 diameters.
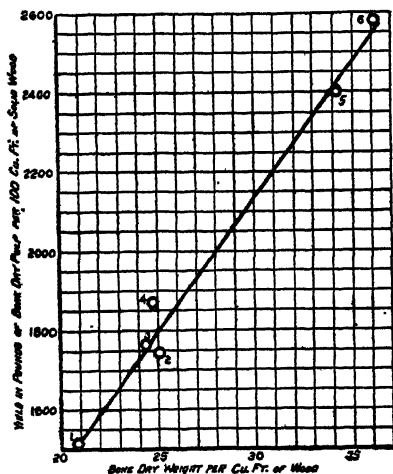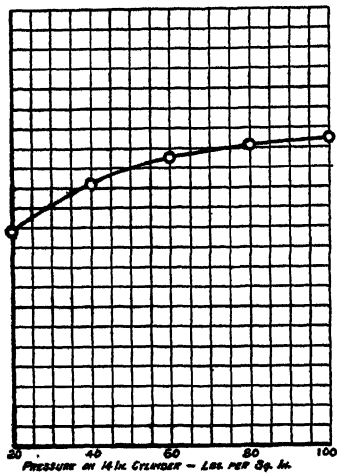
FIGURE 1   FIGURE 2

PLATE 7

Figure 1. Conditions of Tests.
  Speed: 200 R. P. M.
  Pressure: 40 lbs. on 14ᵗ Cylinder.
  Surface: 3 to the inch straight cut
        and 12 to the inch spiral.
  Pockets used: 3 at a time.
  Process: Hot Grinding.
  Wood Treatment: Steamed 8 hrs. at
              60 lbs. pressure.

  Kinds of Woods:
        1. Balsam Fir.
        2. Hemlock.
        3. Jack Pine.
        4. Poplar.
        5. Tamarack.
        6. White Birch.

Figure 2. Conditions of Tests.
  Speed: 225 R. P. M.
  Surface: 3 to the inch straight
        cut and 12 to the inch spiral.
  Pockets used: 2 at a time.
  Process: Hot Grinding.

approximately 50 horsepower per ton. This leads one to believe
that, regardless of the pressure, it would be impossible with the
apparatus used to produce pulp with less than 50 horsepower
per ton in 24 hours.
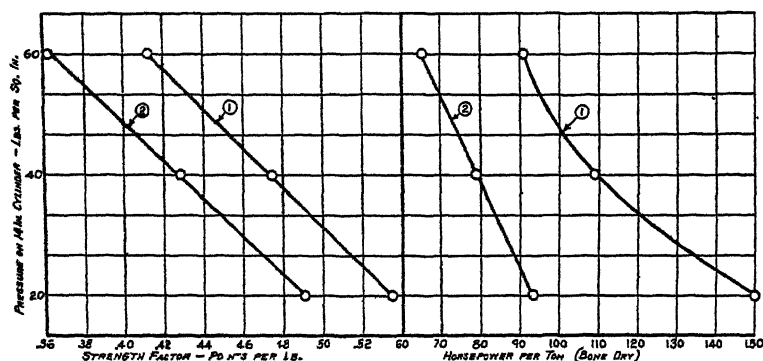
PLATE 8

Conditions of Tests.

Speed: 1. 225 R. P. M.
          2. 175 R. P. M.
Surface: 1.   3 to the inch straight cut and 12 to the inch spiral cut.
          2   6 to the inch spiral cut.
Pockets used: 3 at a time.
Process: Hot Grinding.

YIELD PER CORD AND QUALITY OF PULP

The condition of the surface of stone has very little effect upon the yield per cord of wood. It is true that with extremely sharp stones there are more screenings formed, and possibly more wood fiber finds its way into the white water, but within reasonable limits of sharpness the yield is very slightly influenced.

On Plate 3 are shown two photomicrographs of pulps obtained on stones of different degrees of sharpness. In one case a power consumption of 84.5 horsepower per ton was required, while in the other only 64 horsepower was used. It will be noted that the better quality of pulp is produced at higher power consumption and lower degree of sharpness of stone.

PRESSURE ON GRINDER CYLINDERS

The pressure at which the wood is forced upon the revolving grindstone varies greatly with the diameter and length of the material for any given cylinder pressure. There is liable to be considerable binding of the wood in the grinder pockets also, and this, too, results in a variation of the pressure on the stone. It
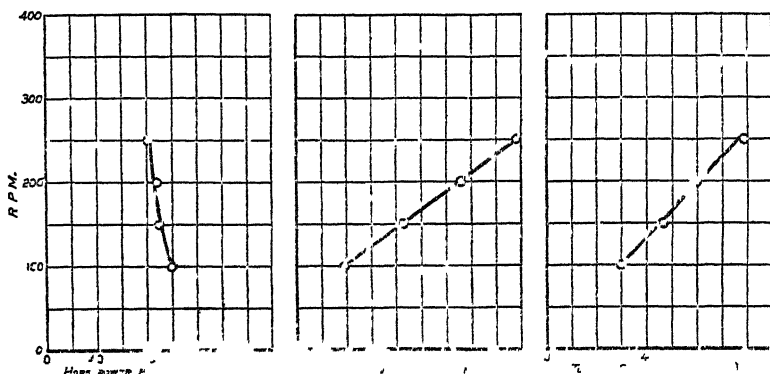
PLATE 9

Conditions of Tests.
    Pressure: No. 60 on 14ᵉ cylinder.
    Surface: 3 to the inch straight cut and 12 to the inch spiral.
    Pockets used: 3 at a time.
    Process: Hot Grinding.

is reasonable to suppose, though, that the variations due to these
factors are fairly constant for any cylinder pressure and conse-
quently do not effect the deductions regarding the relative in-
fluence of different cylinder press res upon factors of economic
production.

Horsepower per ton.   Horsepower to the grinder.
Production in 24 hours.

Plate 4 shows graphically the relations between the pressure
in the grinder cylinders and the horsepower per ton power to
the grinder, and production in 24 hours. The three curves shown
were obtained on surfaces of different degrees of sharpness. It
will be noted that on the stone of greatest sharpness there is a
very slight decrease in the power consumption per ton with in-
creasing pressure and that on the duller stone there is a marked
decrease of power consumption as the pressure is raised. It will
also be noted that the curves converge, thus indicating that it
is impossible to produce pulp at powers lower than a certain
value (approximately 50 horsepower) regardless of the pressure
used in grinding or the surface of stone.

PLATE 10

Conditions of Tests.

Surface: 3 to the inch straight cut and 12 to the inch spiral cut.
Pockets used: 3 at a time.
Process: Hot Grinding.

The power to the grinder varies directly with the pressure on the cylinders as also does the production in 24 hours.

Plate 5 shows the relations between the same factors as on Plate 4.   Here, however, only two pockets in the grinder were used and the pressure was raised to a much higher value.   The decrease in power consumption with increasing pressure will be noted.

As in Plate 4, the power to the grinder and production in 24 hours vary directly with the pressure on the grinder cylinder.

On Plate 6 is shown the relation between the number of pockets used and the horsepower consumption per ton of pulp.   In this test the power to the grinder and the speed were maintained constant, the power being utilized by raising or lowering the cylinder pressure, depending upon the number of pockets used.   It will be noted that when using one pocket corresponding to the pressure of 120 pounds per square inch the horsepower consumption per ton was 58, while when all of the power was used on three pockets, the pressure of 36½ pounds was maintained on each grinder cylinder, and the power consumption per ton was approximately 89 horsepower.   This is only another way of demonstrating that the power consumption per ton of pulp in 24 hours is much lower at high pressure than at low pressure.
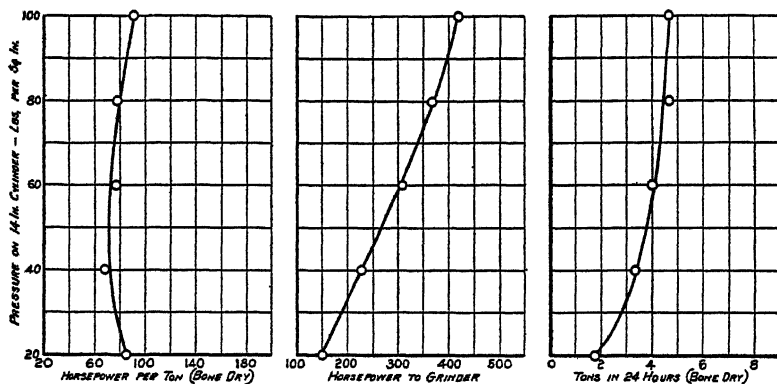
PLATE 11

Conditions of Tests.
    Speed: 225 R. P. M.
    Surface: 3 to the inch straight cut and 12 to the inch spiral.
    Pockets used: 2 at a time.
    Process: Hot Grinding.
    Wood Treatment: Steamed 6 hours at 60 pounds pressure before grinding.

YIELD PER CORD AND QUALITY OF PULP

On Plate 7, Fig. 2, is shown graphically the relation between yield per 100 cubic feet of solid wood and the pressure on the grinder cylinder. It is evident that with increasing pressure the yield of pulp increases. It is true that the amount of screenings also increases, but the gain at higher pressures is due to there being less pulp in the white water.

The effect of pressure on the quality of the pulp, as indicated by the strength of the paper, is shown on Plate 8. Here the strength factor, the bursting strength per square inch divided by the weight per ream, decreases with increasing pressure. The decrease in the strength of paper with the power consumed in making a ton of pulp is also shown.

PERIPHERAL SPEED OF STONE

The peripheral speed of stone is a factor which commercially is in most cases only slightly considered, and rightly. When the pressure on a pocket is removed, unless a governor controls the
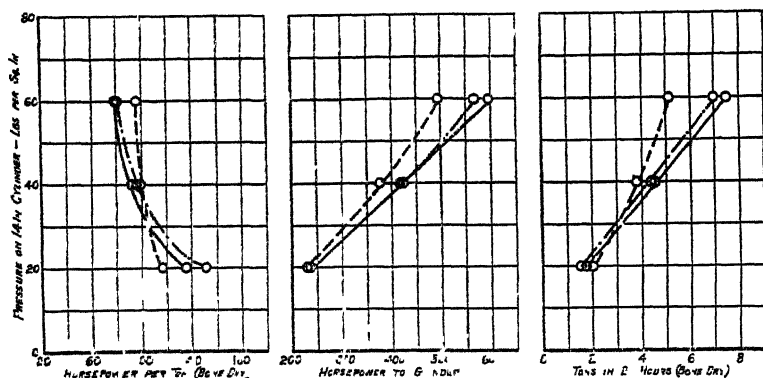
PLATE 12

Conditions of Tests.
    Speed: 225 R. P. M.
    Surface: 3 to the inch straight cut and 12 to the inch spiral.
    Kinds of Woods: Full line.   Green Spruce.
                       Dash and dot.   Seasoned Spruce.
                       Dashed line.   Steamed Spruce.
    Treatment of Wood: Steamed 4 hours at 60 pounds pressure.
    Pockets used: 3 at a time.
    Process: Hot Grinding.

speed, it will increase greatly. The influence of this increased speed, however, is generally more beneficial than otherwise, since it is a means of increasing the production of pulp while only two pockets are in operation.

> *Horsepower per ton.   Horsepower to the grinder.*
> *Production in 24 hours.*

Plate 9 shows the relation between revolutions per minute of the pulpstone and the horsepower per ton, horsepower to the grinder, and tons in 24 hours. It will be noted that with increasing speed the power consumption per ton gradually becomes less, while the power to the grinder and production in 24 hours vary directly with the speed of the stone.

On Plate 10 are shown the relations between the spee   and cylinder pressure and the horsepower consumption per ton,
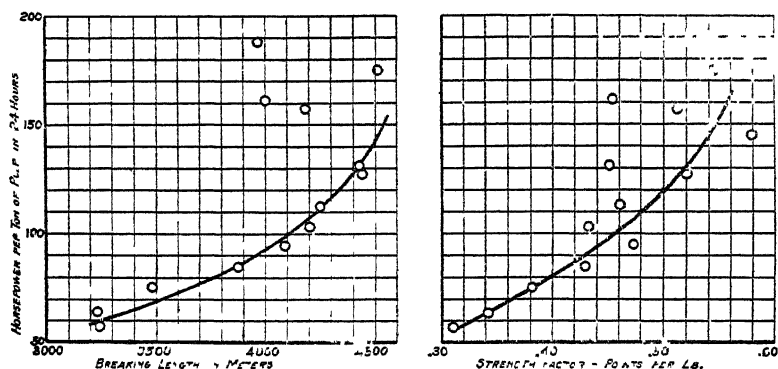
PLATE 13

VARIATION OF STRENGTH OF PAPER WITH POWER USED IN THE MANUFACTURE
OF THE MECHANICAL PULP

Points are averages of 60 values

power to the grinder, and production in 24 hours. In these tests
the power to the grinder was maintained as nearly constant as
possible, the pressure and speed being adjusted to different values
so as to utilize the power in each case. It will be noted that with
constant power to the grinder the production in 24 hours is con-
stant regardless of whether or not the pulp is produced at high
speed and low pressure or low speed and high pressure. It will
also be noted that the power consumption per ton, while increas-
ing slightly with low speed and high pressure, is practically
constant.

YIELD PER CORD AND QUALITY OF PULP

The yield per cord and quality of the pulp are only influenced
slightly by the speed. The yield appears to be somewhat higher
with high speed production. The difference, though, over low
speed production is small. The quality, as determined by strength
tests of paper made from the pulps, is not influenced in a regular
manner as it is by the pressure of grinding.

THE MOISTURE CONTENT, WEIGHT PER CUBIC FOOT, AND CONDITION OF THE WOOD

The question of the influence of moisture content and condition
of the wood is a very important one. Wood for pulp purposes is

almost invariably allowed to season for a long period before using. As a result it becomes dark colored and will not yield the long fine fibers which can be obtained from green wood. The treatment of wood prior to grinding, by steaming, boiling or some other like process, is important also because by this manner of treatment better fibers can be obtained from wood which, when ground in the natural state, yields pulps which are very short fibered. In this way, too, pitchy woods are made usable by the mechanical process.

Horsepower per ton.   Power to the Grinder.
Production in 24 hours.

On Plate 11 is shown graphically the relations between the pressure of grinding and the power consumption per ton, power to the grinder, and production in 24 hours when the wood used had been steamed prior to grinding for 6 hours at a steam pressure of 60 pounds per square inch. It will be noted that the power consumption per ton is a fairly constant quantity and that there is a decided contrast between values of power consumption, power to the grinder, and production in 24 hours obtained on steamed wood and values obtained on seasoned untreated wood as given on Plate 6.

The power to the grinder under like conditions of speed and pressure is much less when steamed wood is used than when the wood is unsteamed, and this is also true of the production of pulp in 24 hours.

On Plate 12 is shown the relation between the pressure on the grinder cylinders and horsepower consumption per ton, power to the grinder, and production in 24 hours. These tests were conducted using green, seasoned, and steamed wood. It will be noted that the power consumption generally is lower for seasoned wood than for steamed wood, and still lower for green wood than for either seasoned or steamed wood.

The power to the grinder required for either seasoned or green wood under like conditions of speed or pressure is essentially the same. The power is less, however, when steamed wood is used, this undoubtedly being due to the lubricating action of the steamed material.

It will be noted that the production of pulp from green wood is greater than from seasoned wood; also that the production of steamed wood is less than for either of the other two materials.

YIELD PER CORD AND QUALITY OF PULP

The yield per cord is much less when the wood is given a steaming treatment than when it is ground in the natural state. However, practically the same amounts of pulp can be obtained from green or seasoned wood when produced under the same conditions of grinder operation. The thing which most influences the yield is the bone-dry weight of the wood. On Plate 7, Fig. 1, is shown graphically the relation between these two factors. It will be noted that the yield of pulp is directly proportional to the bone-dry weight of the wood; in this case different kinds of woods were used in the tests.

The quality of the pulp can, of course, only be measured by its suitability for use in different paper. The pulp produced from steamed wood is dark in color but very strong. That produced from very dry wood is invariably of shorter fiber and darker color than that obtained from green wood under like conditions. However, the green wood contains more pitch and this may cause trouble in the operation of the paper machines.

TEMPERATURE OF GRINDING

The temperature of grinding has almost no influence upon the power consumption per ton, power to the grinder, or the production in 24 hours. Likewise it does not seem to influence the yield from a cord of wood. The quality, in so far as strength and toughness are concerned, is influenced, pulp of better quality being obtained under conditions of hot grinding. In this case, as in others, however, the measure of quality is the adaptability of the pulp to use in the desired sheet of paper and it is unquestionably true that for certain purposes pulp produced by the cold grinding process is more desirable than that of the hot process.

INFLUENCE OF POWER EXPENDED IN PULP MANUFACTURE ON THE STRENGTH OF PAPER MADE THEREFROM

There is shown graphically on Plate 13 the relation between the power consumption per ton of mechanical pulp in 24 hours

and the strength factor and breaking length of paper made from the pulp. The results here plotted are the averages obtained under many different conditions of surface of stone, pressure, speed, temperature, etc. It is evident from this curve that in order to make strong paper it is necessary to consume considerable power in the manufacture of the mechanical pulp. This, of course, does not take into consideration the possibilities of refining processes. The strength factors shown, even for pulps of low power consumption, are equal to or greater than values obtained for newspaper in commercial practice. This may be due, however, to the fact that a small paper machine and much care were used in the manufacture of the paper; also to the fact that the strength tests were made on uncalendered paper.

CONCLUSIONS

1. The power to the grinder increases directly with the speed and pressure, and inversely with the degree of sharpness of the stone. There is also a very slight increase with the temperature. Under like conditions of all other factors the power to the grinder is less for steamed wood than for green or seasoned wood untreated.

2. The production of pulp in 24 hours varies directly with the pressure, speed, and the degree of sharpness of the surface of stone. Less pulp is obtained in 24 hours from seasoned wood than from green, and still less from steamed wood, all other conditions being the same.

3. The horsepower consumption per ton on untreated wood increases as the pressure decreases according to a fairly definite law; it is lower on sharp stones than on dull and it increases as the speed decreases in much the same manner as is the case with pressure. There is, however, not as much difference between the power consumption per ton at low speed and at high speed as there is between power consumption at low pressure and high pressure. The temperature has very little influence on power consumption; it is slightly lower at high temperatures. The power consumption per ton is higher for seasoned wood than for green wood, and still higher for steamed wood than for either seasoned or green wood ground under the same conditions. Conifers require more power per ton of pulp produced than hard woods.

4. The yield of pulp per cord is greater at high pressure than at low, and this is also true of screening. There is, however, not as much fine material lost in white water when high pressure is used. The surface of the stone does not greatly influence the yield per cord. The yield is slightly higher at high speed than at low and it is directly proportional to the bone-dry weight per cubic foot of wood.

5. The quality varies greatly with the surface of the stone, less greatly with the pressure, and least with the speed. The weight per cubic foot and character of wood influence it to a marked extent, especially the latter. The temperature has a marked influence, pulp of higher quality being obtained at higher temperature. Pulp of better color can be obtained from green wood than from seasoned, and stronger pulp can be obtained by steaming the wood prior to grinding. The quality of paper produced under exactly the same conditions but made of pulps produced at different grinder pressures varies directly with the grinder pressure and the horsepower consumption per ton of pulp. Pulp of highest quality can only be produced from a definite kind of wood by the expenditure of a large amount of power.

Abstract

ESTIMATION OF CELLULOSE. CELLULOSE METHODS VERSUS CRUDE FIBRE (ROHFASER) METHODS

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In a series of articles published in the Zeitschr: Farb: Ind. vols. 10–11 (1911–1912) are set forth the results of elaborate experimental investigations by the authors, J. König and Fr. Hühn, with their general conclusions as to methods of isolating and estimating cellulose.

They advocate "Rohfaser" or "Crude Fibre" methods followed by specific oxidising treatments for removal of lignone residues, and dismiss the "cellulose" methods, notably those more generally adopted—viz., chlorination (Cl. Aq, Cross & Bevan), Bromination (Br Aq, H. Müller), since they yield according to the authors, heterogeneous mixtures of true cellulose ["wahre cellulose"] pentosanes, furfuroids, and hemi-hexoasanes.

It has been deemed opportune to submit this communication to critical analysis, as it seeks to assail the foundations of cellulose technology as generally accepted, and to reverse the judgment of the sub-committee on analyses which reported to the Seventh International Congress (London).

It is now shown that the "residues" which the authors obtain either by their process, which is selected in the first place, or by that of Tollens and Dmochowski, also a "Rohfaser" method, proposed in the second place, are advanced products of decomposition and disintegration.

They have no claim to be regarded as celluloses, and the confusion of such products with "cellulose" not only obscures the natural relationships of the celluloses, but leads the authors into a number of mistakes both of experimental numbers, as of interpretations of numerical results correct in themselves.

The most prominent of these are pointed out and discussed.

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A fundamental error is to regard, as they do, the chlorination process as a process of oxidation.

On this point some special experimental work is now recorded in which the two processes of attack of lignone residues, *viz.*, by Cl Aq and by Br Aq are contrasted.

In the latter case the action of the halogen is in effect complicated by oxidations, which under severe conditions of action are considerable in relation to the degree of bromination.

In the case of chlorine gas, the minimum of secondary action (oxidation) is further reduced under special conditions of reaction, *viz.*, absence of light and low temperature.

The authors have no hesitation in anticipating the judgment of competent critics of this attempt to substitute the present methods of cellulose estimations, by methods based on the "Rohfaser" of the agronomic chemists.

The former are based on the natural perspective of the celluloses, as (1) products of plant life, (2) the basis of our most important manufactures and (3) chemical individuals defined by laboratory methods both statistical and constitutional.

The "Rohfaser" residues are products of degradation by treatments more or less arbitrary, because relatively non-selective in their actions, which are moreover ill-defined through the complex and unascertained relation of products to the mother substances.

Further, the particular process commended by the authors involves long, drawn-out manipulations out of all relation to the exigencies of technical investigations.

Both on practical as well as scientific grounds, therefore, the authors fail to justify their attack upon a position based upon "natural science" and the accumulated experiences of a generation of scientific and industrial technologists.

ANTISEPTIC TESTS OF WOOD PRESERVING OILS

By A. L. Dean and C. R. Downs

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The materials commonly employed for impregnating wood for the purpose of preventing its decay fall readily into two classes, —soluble salts and hydrocarbon oils. The most widely used member of the first group is zinc chloride, and of the second, coal tar creosote. Ever since the introduction of this last named material by Bethell in 1838 it has been employed in constantly increasing amounts, and today creosoting—properly performed— is regarded as the most effective method of timber preservation.

In recent years the large demand for coal tar creosote and the rather high cost of the treatment with the amounts considered necessary, have led to the use, openly and otherwise, of other materials. Thus the heavy asphaltic petroleum oils have been tried to some extent, notably in the treatments by the Santa Fe railroad where sufficient of the oil has been injected to render the wood well-nigh waterproof. The oil distilled from the tar resulting from the manufacture of carburetted water gas has been used to a considerable extent, but since its value was uncertain it has been regarded as an adulterant or substitute for the oils distilled from coal tar. Water gas tar shows many points of similarity to coal tar, and the creosote oil distilled from it is very like that distilled from coal tar, although it contains neither the phenols nor the nitrogenous bases characteristic of the latter. Inasmuch as large quantities of water gas tar are produced at the gas works in the United States, and the creosote distilled from it might readily be had in substantial amounts, it is important to arrive at a sound estimate of its value as a timber preservative.

The qualities commonly desired in a wood preserving oil are freedom from loss by volatilization, solution or chemical change, and a marked toxicity to wood rotting fungi and the animals which destroy timber.

In volatility, solubility and chemical inertness water gas tar

creosote compares favorably with the oils from coal tar; the relative antiseptic powers of the two classes of oils is less readily determined. The present communication outlines the results of a laboratory study of the antiseptic powers of oils prepared from coal tar and water gas tar, and is designed to assist in arriving at a proper estimate of the place that water gas tar oils should occupy in timber preservation.

The value of water gas tar creosote as a wood preservative has been the subject of some controversy, but as yet the amount of reliable data has not been large. Practical tests on a commercial scale giving the results of the test of time under service conditions have not been carried out. Where the material has been used it has usually been employed in mixture with coal tar creosote, sometimes without the consumer's knowledge. The result has been that in the absence of reliable information consumers have preferred to rely on coal tar creosote of the value of which they were certain.

Alleman[1] has studied the character of the oils remaining in timbers which, after being treated with coal tar oils, have been many years in service. The results show that the low boiling oils present in creosote disappear after a number of years of service, and the tar acids or phenols are no longer present. There has been in recent years a growing tendency to regard these high boiling hydrocarbon oils such as Alleman found remaining in his well preserved timbers as the most valuable constituents of creosote oils.

During 1911 J. M. Weiss[2] presented two papers to the New York Section of the Society of Chemical Industry dealing with the antiseptic value of the oils and tars used in timber preservation. These papers showed the relative antiseptic value of coal tar oils and water gas tar oils under the conditions of Weiss' experiments, as well as furnishing some information on the relative values of the different tar oil constituents. These papers furnish the most important experimental evidence of the antiseptic powers of the

[1]Gellert Alleman. Circular 98, Forest Service of the U. S. Department of Agriculture, May, 1907.

[2]J. M. Weiss. Journal of the Society of Chemical Industry, Feb. 28, 1911, p. 190, and Dec. 15, 1911, p. 1348.

different oils. The work of Weiss showed that coal tar creosote was many times as toxic to the organisms used in his experiments as the water gas product, and that the lower boiling coal tar oils were distinctly more antiseptic than the heavy high boiling ones.

Two criticisms may be made of the methods employed by Weiss. The first, and less important, being that the fungi used by him to test the antiseptic powers of the materials experimented on by him were not wood destroying fungi and their powers of resistance to various agents might not be the same. A much more serious objection to his results depends upon the method employed in preparing the media containing the oils to be tested. These are for the most part insoluble in water, and being heavy, sink rapidly to the bottom of the containing dishes, so that a uniform distribution of the oil is not effected, and the cells of the fungi may not come in contact with it. It is apparent that oils containing water soluble constituents would partially dissolve and prove more antiseptic than the more insoluble oils. It might readily be that the relatively greater antiseptic power of the lighter coal tar oils was partly due to solubility of the phenols present in them, the toxic power of which is well known. It would seem that a much fairer idea of the antiseptic power of the oils tested could be gained if they were uniformly distributed throughout the culture medium so that the fungus must come in contact with them.

The organism used in the experiments to be described was *Polystictus versicolor* obtained in pure culture from wood decaying through the action of this fungus and tearing masses of its sporophores on the surface. Numerous cultures were kept in the laboratory on small blocks of sterilized *Liriodendron* wood on which it grew readily, and which it reduced to about the specific gravity and strength of pith in the course of a few months. There was no doubt of the purity of the cultures nor of the powerful attack of the fungus on the wood. This species was used because of the readiness with which it may be isolated in pure cultures which grow vigorously under laboratory conditions, and also because it is one of the most important enemies of structural timber in the United States. Von Schrenck[1] says of this species:

[1]Von Schrenck. Bulletin 149, Bureau of Plant Industry of the U. S. Department of Agriculture, p. 53.

"Of all the fungi which grow upon the deciduous species of woods after they are cut from the tree, the most widely distributed and in many respects the most destructive is *Polystictus versicolor*.... On account of its wide geographical range and its ability to grow on and destroy so many different kinds of wood it should be regarded as the most serious of all the wood-rotting fungi which attack the dead wood of broadleaf trees. It is the fungus which destroys probably 75% or more of the broadleaf timber used for tie purposes."

Inoculations into the media to be tested could not be conveniently made from cultures growing on wood and transfers were therefore made to prepared agar from which the fungus could be readily cut and small masses of the mycelium transferred by the use of a small piece of platinum foil set in a glass handle.

The culture media were prepared in the following manner. Ordinary white beans (*Phaseolus vulgaris*) were germinated in a dark place until several inches high. The seedlings were then ground up in a meat chopper and a boiling water extract of them made. Due to the chemical changes characteristic of the process of germination some of the starch of the beans is hydrolysed to dextrins and sugar, and much of the nitrogen present as the proteins of the seeds appears as soluble cleavage products in the seedlings. One-half of one per cent of cane sugar and a like quantity of asparagin were added to the germinated bean extract to supply further nourishment. This medium was then stiffened by the addition of 1.5% of agar agar, and 10 cc. portions of it pipetted hot into 22 mm. test tubes, plugged with cotton and sterilized.

A five-gram portion of each of the creosote oils to be tested was weighed out into a mortar containing an equal weight of powdered gum arabic and the two rubbed well together. Water was then added a little at a time with constant grinding, yielding an emulsion containing as the emulsifying agent a carbohydrate material similar to the agar agar of the medium. The emulsion was diluted with water to 100 cc., making a 5% emulsion which would not separate even after several months of standing.

Portions of these five per cent emulsions were measured into the 10 cc. portions of the sterilized agar medium with a pipette

graduated to hundredths of a cubic centimeter. As a rule three test tubes of each strength were prepared in order to check the results. The agar was then melted and the tubes well shaken in order thoroughly to mix the emulsion with the medium, and then quickly cooled under cold water in a slanting position. In this way the oil was uniformly distributed throughout the medium in the form of finely divided globules and held permanently in position by the solidification of the agar.

In the first series of tests the oils used were a very good grade of commercial coal tar creosote, a water gas tar creosote made in the laboratory by taking the fraction distilled from 170° to 340°C. from a sample of water gas tar of known origin, and a sample of pressed anthracene oil. The results of the fractional distillation of the two first samples are given in the table below.

Temperature	Coal tar creosote	Water gas tar creosote
170°C.	0.2%	5.5%
170° 205°	6.3%	4.5%
205° 240°	30.7%	35.5%
240° 300°	21.3%	32.5%
300° 320°	9.1%	6.0%
320° 340°	13.5%	

The coal tar oil contained 8% of tar acids. The anthracene oil was a commercial product, 50% of which distilled between 250° and 350°C. The solids had been pressed out, leaving it liquid at room temperatures.

The strengths of coal tar creosote tested varied by .05% increments from .05% to .35%, and of the other two oils from .05% to .75%.

The results of this preliminary series indicated an inhibition point for the fungus with .25% of coal tar creosote, .40%–.45% of the water gas tar creosote, and over .75% for the pressed anthracene oil. In the case of the last named material the growth became progressively weaker, but was not entirely inhibited at the highest concentration tried.

One serious difficulty developed in the tests. In transferring the fungus mycelium to the test tubes it was necessary to cut out a small piece of the agar of the stock culture and it was almost

impossible to tell whether the fungus was growing slightly on the creosoted agar or whether all the growth was derived from the small piece of transferred medium. This led to some uncertainty as to the precise point at which growth was inhibited. In the second series, this was remedied by cutting out a small piece of the medium to be inoculated with a sterile platinum foil, laying the cut out piece over to one side, placing the transferred mycelium and agar from the stock culture in the cavity, and then replacing the piece of creosoted medium on top of the transferred material. In this way the mycelium used for inoculation was buried within the mass of material to be tested and if it grew up through it and vegetated at the surface there could be no question that the antiseptic was insufficient to prevent the growth of the fungus. The control cultures were made in the same manner.

The too rapid drying out of the cultures noticed in the first series was prevented in the second by placing them in a large glass walled case with a water saturated atmosphere.

Since the fungus used in the first series might have had its vitality somewhat impaired by being kept so long in artificial cultures, new samples of wood decaying through the action of the organism were found and fresh pure cultures prepared and used for inoculating the second series of tests. The following oils were tested.

A. Coal tar creosote No. 1.

B. Coal tar creosote No. 2, prepared in the laboratory by taking the fraction distilling from 200° to 350°C., from a sample of coal tar; since there was a considerable separation of napthalene in this sample on cooling to room temperature. which rendered it impossible to make a satisfactory emulsion, the solids were filtered off.

C. Water gas tar creosote No. 1.

D. Water gas tar creosote No. 2, prepared in the laboratory by taking the fraction distilling from water gas tar between 200° and 350°C., yielding a sample somewhat heavier than the No. 1 and comparable in boiling range with coal tar creosote No. 2.

E. The same sample of pressed anthracene oil used in the first series.

F. Coal tar creosote No. 1, washed with alkali until free from tar acids and then washed with water.

G. A portion of F. with the tar bases removed by treatment with sulphuric acid, and washed with water.

An attempt was made to make emulsions with anthracene and napthalene for antiseptic tests in the manner described above for the oils, but was found impossible to make satisfactory emulsions. The attempted stock emulsions of these materials containing about 5% of the hydrocarbons stood for some time in the laboratory and it was noted that a mould growth appeared on the surface. The napthalene and anthracene had settled to the bottom. This observation would tend to support the statement made by Weiss that these materials were not antiseptic up to 10%. This conclusion seems not to be wholly justified, however, because the mould was not in contact with the hydrocarbons.

The results of the tests in the second series were as follows:

Sample	Inhibition Point
A. Coal tar creosote No. 1	Below .4%
B. Coal tar creosote No. 2	.4%
C. Water gas tar creosote No. 1	.4%
D. Water gas tar creosote No. 2	.35%
E. Pressed anthracene oil	Above .85%
F. Sample A. minus the phenols	.30%
G. Sample A. minus the phenols and tar bases	Above .6%

In the case of sample E. there was a gradual weakening of the growth from .2% to .85% which was the highest concentration tried, and a similar state of affairs developed in the tests of sample G., the highest strength of which was .6%. Of the two the cultures with sample E. were slightly the more vigorous.

From these results it is evident that coal tar creosote is a stronger antiseptic than water gas tar creosote, and that water gas tar creosote is distinctly more effective than the liquid oils of the anthracene fraction of coal tar. The greater value of the coal tar oil appears to depend upon the presence of the tar acids and especially upon the tar bases. It is interesting to note that the water gas tar creosote was almost identical in antiseptic power with the coal tar oil with its tar acids removed.

The work of Alleman cited indicated that the oils remaining in wood treated with coal tar creosote are almost free from

tar acids after a few years of service, and that under conditions a lowing evaporation the lighter hydrocarbons are nearly all lost. Loss of antiseptic power from the disappearance of the tar acids cannot take place with water gas tar oils, since they are free from phenols in the beginning.

Since the amount of creosote injected into wood is commonly 10 pounds per cubic foot or more, it would appear that the difference in antiseptic value between coal tar oils and water gas tar oils is not of great significance, especially in view of the probable disappearance of the tar acids from the wood treated with coal tar creosote.

On the basis of such data as we have it seems justifiable to conclude that the oils distilled from water gas tar have a distinct value as wood preservatives, and that there is no reason why they should not be purchased and used under their own names with no attempt to masquerade as coal tar products.

THE PRESENCE OF MALTOSE IN ACID HYDROLYSED STARCH PRODUCTS

By GEO. DEFREN

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Earlier discussions about the hydrolysis of starch by acids assumed the presence of maltose as one of the intermediate products between soluble starch and dextrose.

Maltose is formed usually by the action of diastase on starch. This maltose can be easily hydrolysed to dextrose by acids; and, as dextrose was the final normal product of acid hydrolysis of starch, it was natural to assume that maltose must have been an intermediate product.

The fact that the curve representing the cupric reducing powers at various rotations is an arc of a circle, and, at its centre, lies considerably above the chord limiting the beginning and the end of the hydrolysis as produced by acids, indicates that some other influence, in addition to that of dextrose, is a factor in producing the curve, and this has been attributed to maltose.

Effort[1] had been made to separate the maltose by eliminating the dextrin by precipitation with alcohol. This was a difficult undertaking, as dextrose was also somewhat soluble in alcohol, and the phenyl-osazones melt only one degree C. apart. Crystals corresponding to phenyl-maltose-azone were obtained, but free maltose had not been isolated.

It occurred to the author to try a different method. As dextrose had to be eliminated—as well as any dextrin present—it was determined to ferment this hexose from the mixture. Advantage was taken of the fact that sac. apiculatus ferments dextrose, but not maltose—or, at any rate, the latter less actively.

As acid hydrolysed starch products have varying percentages of carbohydrates at different optical rotations, it would be advantageous to select a mixture which would have maximum maltose present. This should be theoretically between $[a]_D$

[1]Jour. Am. Chem. Soc. 25, 1015.

150° and $[a]_D$ 110°.   A high rotating glucose of $[a]_D$ 150°   would have little dextrose to ferment, but much dextrin to eliminate by precipitation, while a mixture at $[a]$ 110°   would have much more dextrose, but only one-third as much dextrin.

A product of $[a]_D$ 144°   was first taken, yeast water, and ammonium phosphate added, then impregnated with sac. apiculatus and fermented.   The alcohol was removed by distillation, and the remainder again subjected to fermentation.

The residue was concentrated, poured into a large volume of boiling 90% alcohol, and the precipitate allowed to settle.   The supernatant liquid was filtered, concentrated to a thick syrup, and its contents allowed to crystallize.   The dark, thick crust was redissolved in boiling water, decolorized with bone black, and again crystallized.   The final product was a white crystalline powder which showed all of the physical properties—optical rotation, copper reduction, and formation of osazone—characteristic of maltose obtained heretofore only by the action of diastase on starch.

Fermentation experiments were also made with an acid converted starch product of $[a_{[D}$ 110°.   This gave the maltose more easily than did the glucose of 144°, probably owing to the fact that there was much less dextrin to eliminate by alcohol precipitation.

This isolation of pure maltose thus puts an end to the oft repeated contention that dextrose only results from the action of acids on starch.

THE HYDROLYSIS OF STARCH BY ACIDS, WITH SOME ADDITIONAL RESULTS ON THE SPEED OF HYDROLYSIS

By Geo. Defren

Newton, Mass.

Commercial analyses of malt worts and similar products of the action of diastase on starch are based on the assumption that but two simple compounds are formed—maltose and dextrin. In the case of glucose-starch syrup and starch sugars, which are the product of acid hydrolysis, it is known that the reaction proceeds further, and that dextros (d-glucose) is formed.

Investigation has shown that all of these compounds are present in the solutions produced by acid hydrolysis of starch, and that consequently the reactions forming them must have gone on together. Evidently there are quite a number of intermediate products—molecular complexes—of dextrin and maltose[1], which have different optical and copper-reducing powers, and have different coloring properties with iodin.

It has been shown[2] that at any stage of the conversion of starch by diastase, the total product in its optical properties, and relation to Fehling's Solution, behaved exactly as if made up of two components only—dextrin and maltose—so that it was possible by taking the rotatory power, to calculate at once the reducing power, if the weight of the total carbohydrates were known. This law indicated that, however complicated the bodies isolated, they could be considered as existing in solution as two simple substances, and did much to establish the principles of the usual commercial analyses of worts and similar products.

The methods of analysis of glucose syrups and starch sugars implied the assumption of a similar law, such has been shown to be the case.[3] A large number of conversions of starch were made under varying conditions of temperature and concentration of

[1]Ber. d. Chem. Ges. 28. 1522–1531.
[2]Am. Chem. (Liebig) 231, 131.
[3]Jour. Am. Chem. Soc. XVIII. No. 10.

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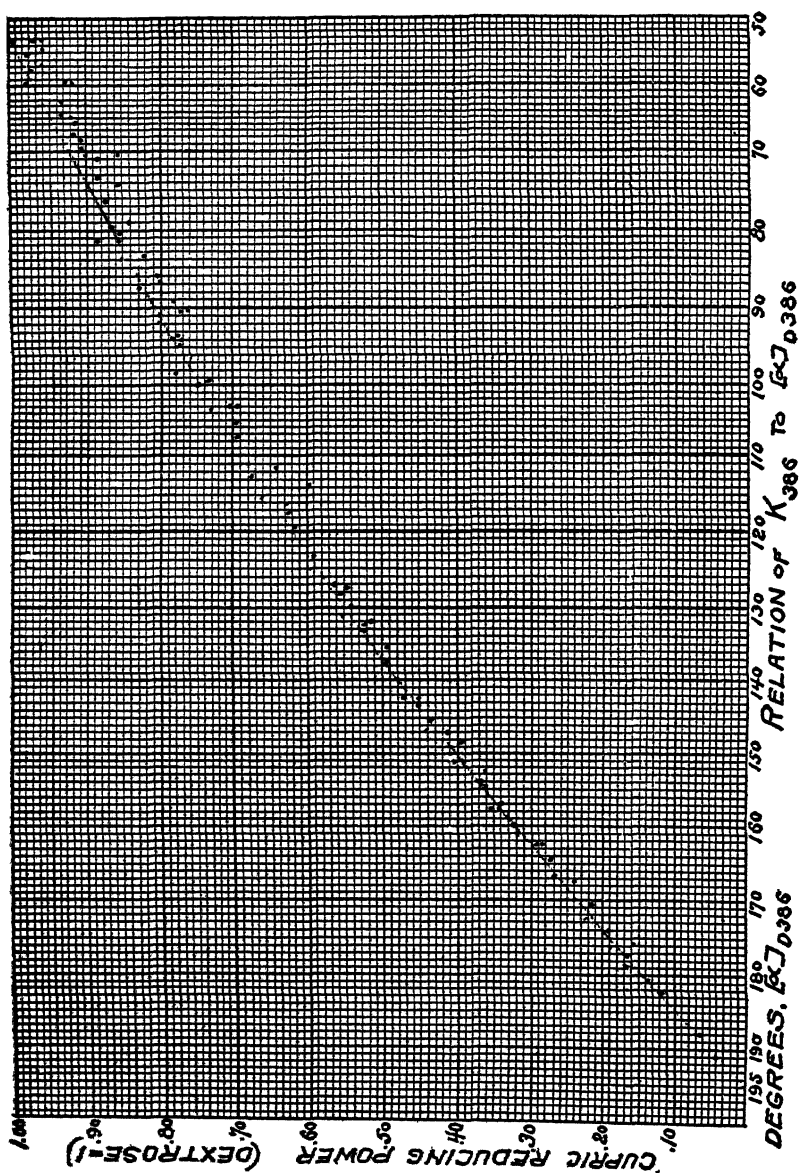
different acids, but the results were invariably the same. In other words, the values obtained pointed to the remarkable fact that the cupric reducing power of the total product bears a constant relation to the specific rotatory power, even when the starch has been hydrolyzed by acid under widely varying conditions. Hence, given the one, the other could be calculated.

The relations between the optical rotations and the cupric reducing powers are shown graphically in Plate A.

The upper part of the curve is not so well defined, the results showing more discrepancy at the high conversion stages. This may be due to some decomposition, or so-called "reversion products."[1] That the solutions begin to color considerably beyond 90, is, moreover, a strong indication of such decomposition.

By taking the optical properties [a] and the reducing powers (k) of dextrin (d), maltose (m), and dextrose (g), in acid hydrolyzed starch mixtures, we get several equations. The results are given graphically in Plate B.

[1]Ber. d. Chem. Ges. 231, 2101.
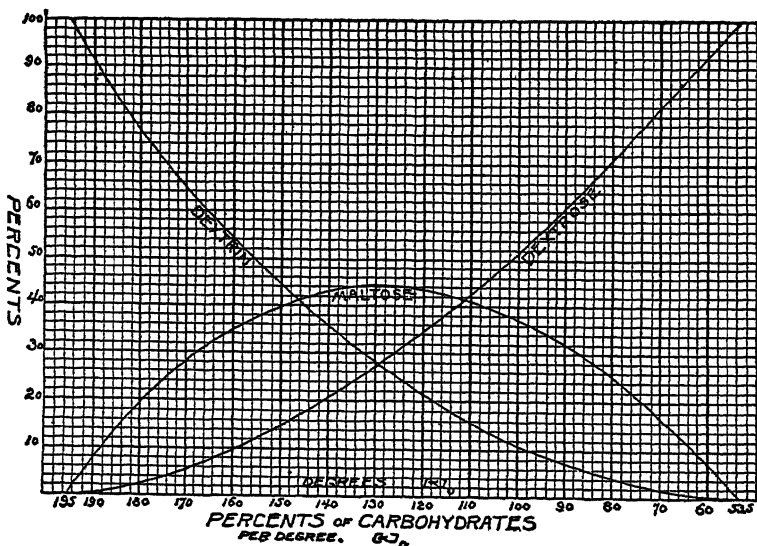
PLATE B

Examining these curves, we see that dextrin, starting from a maximum of 100%, gradually falls to "zero" near the rotation corresponding to that of dextrose. The percentage of maltose gradually rises, reaches a maximum of 46.2% at about $[a]_D$ 129°, corresponding to the usual state of commercial glucose-starch syrup—and then falls, disappearing at 53.5°. The dextrose, on the contrary, steadily mounts to 100%.

These plots do not take into consideration the presence of any decomposition products which are evidently present in slightly increasing amount between the rotations of $[a]_D$ 90° and $[a]_D$ 53.5°, to which reference has already been made. Some investigations have already been undertaken concerning these decomposition products, but as yet with no tangible results.

To summarize the above results: We find that starch is first liquefied by boiling water, forming the so-called "starch paste," or amylo-dextrin, which colors iodin deep blue. In the presence of any acid which dissociates in water solution, this amylo dextrin is hydrolyzed, taking water into the molecule, and producing complexes of dextrin, and maltose, and called, collectively, "malto-dextrins." These have varying optical and copper reducing powers and are effected differently by iodin, those of higher molecular weight giving blue or violet colorations and changing gradually into dark red or brown, then going over into yellow, and finally becoming colorless when the rotation falls below $[a]_D$ 140°. Further addition of water to the molecule results in the formation of free maltose, which is itself then hydrolyzed into dextrose by the addition of another molecule of water. Dextrose is, then, the final normal product of the hydrolysis of starch by acids.

THE SPEED OF HYDROLYSIS OF STARCH BY ACIDS

The development of physical chemistry in recent years has shown that the hydrolysis of substances in solution by acids is due to the action of the dissociated hydrogen ions of these acids. Assuming that the amount of acid and the temperature remained constant, the rate of inversion at any specified moment is proportional to the amount of unchanged substance present at that moment. That has been proved to be the case with cane sugar, salicin, and many other substances.

The observations noted above suggested the possibility that in the hydrolysis of starch the acids should show the same proportionate speed of reaction. This is an especially interesting problem because the starch molecule is exceedingly complicated, the molecular weight being undoubtedly very high. Some work which we have done has shown results above 33,000.

Starch hydrolysis, however, must be considered as somewhat different from that of cane-sugar or salicin. While these latter are easily soluble in cold water, starch is totally insoluble at ordinary room temperature. On the other hand, amylo-dextrin, the product of decomposition of starch by boiling water, is somewhat soluble in cold water, its solubility increasing with rising temperature.

As by the customary procedure in determining speed of hydrolysis, it would be necessary to ascertain the exact moment when all the starch has been converted into soluble form, a point not conveniently determined, a method of measurement based on the following principles has been adopted.

The conversion products of starch, with the possible exception of those of very high rotatory power, are easily soluble in water, and can be looked upon as mixtures of dextrin, maltose, and dextrose. The starch first changes to amylo-dextrin; this then goes over into maltose and finally dextrose is formed. The dextrin may, therefore, be looked upon as the original substance hydrolyzed, the maltose and dextrose as successive products of the reaction. Further, it has been shown that whatever the condition of the hydrolysis of starch by acids, the specific rotatory power of any conversion product corresponds to a definite chemical composition, tables for determining which have been constructed.

Thus, for instance, a conversion product of $(a)_D$ 160° has been shown to contain 54% dextrin, the remainder being maltose and dextrose. Hence the time of taking any sample after the contents of the autoclave have reached a constant temperature, which requires about 10 minutes, can be taken as the initial point for determining speed of hydrolysis and all subsequent samples referred to this, as it is obvious that in any sample we can ascertain the dextrin unacted upon at that stage of the hydrolysis. The same holds true of maltose.

We have to deal with two reactions, the first being the hydrolysis of dextrin to maltose.

If A° is the amount of dextrin at the initial point taken, $A^\circ - x$, the amount remaining at any time t, and c, the constant depending on conditions of hydrolysis we get $\dfrac{dx}{dt} = c\,(A_0 - x)$.

This, on integrating gives nat. log. $\dfrac{A_0}{A_0 - x}$ ct, or $\dfrac{1}{t} =$ nat. log. $\dfrac{A_0}{A_0 - x} = C$, which is the general equation of a first order reaction.
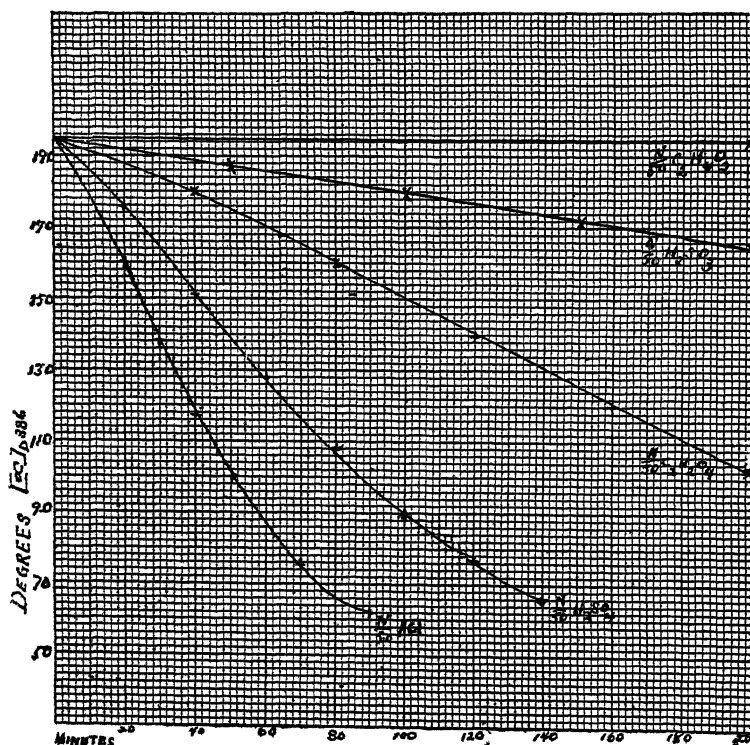
PLATE C.

INFLUENCE OF VARIOUS ACIDS

PLATE **D.**

(INFLUENCE OF STRENGTH OF ACID AT, 4 AT(145°C).
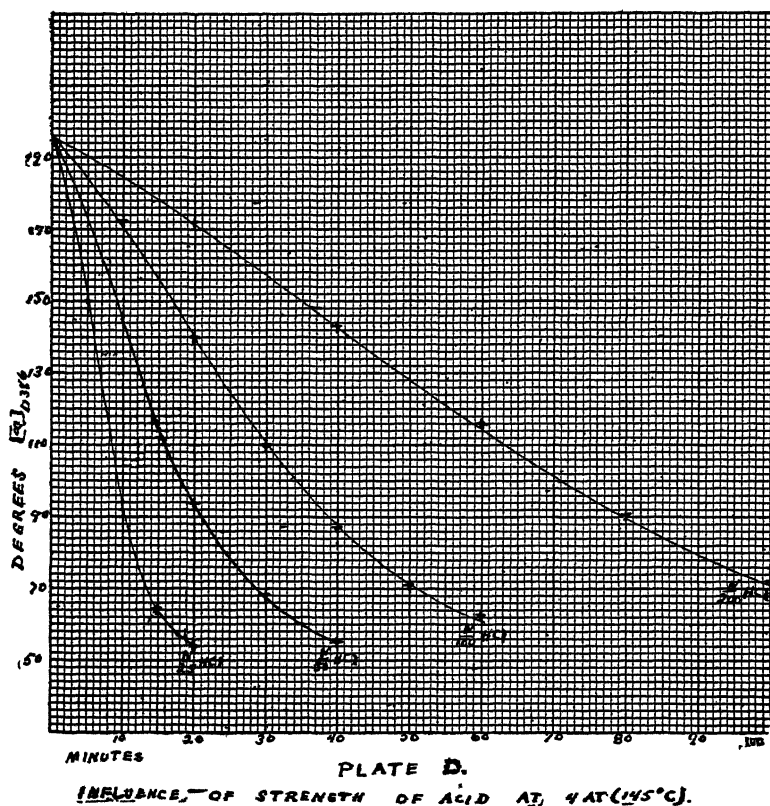
The second decomposition is that in which maltose is hydrolyzed to dextrose, and is peculiar in so far as it proceeds simultaneously with that reaction expressed by the equation above. Consequently the equation expressing accurately the rate of change in the total amount of maltose present is quite complicated, and this has lead to the use of an approximate formula, which is sufficiently exact for the work in hand. The formula is derived from the exact differential equation $\dfrac{dD}{dt} = CM$, which states that the amount of dextrose formed at each moment is proportional to the amount of maltose present, by replacing the differential

quantities by finite differences, which, in application of the formula, must of course be taken small. In the place of M, the average amount of maltose present during the interval of time considered is also substituted. That is, if M_1 and M_2 are the amounts of maltose present at the times t_1 and t_2, and D_1 and D_2, the amounts of dextrose present at these same times, and c_1 the reaction constant, we get as a result of the above-mentioned substitutions:

$$D_2 - D_1 = c_2 \frac{M_1 + M_2}{2} (t_2 - t_1), \quad C_1 \left(\frac{1}{t_2 - t_1} \right) \left(\frac{D_2 - D_1}{\frac{M_1 + M_2}{2}} \right) = C_2.$$
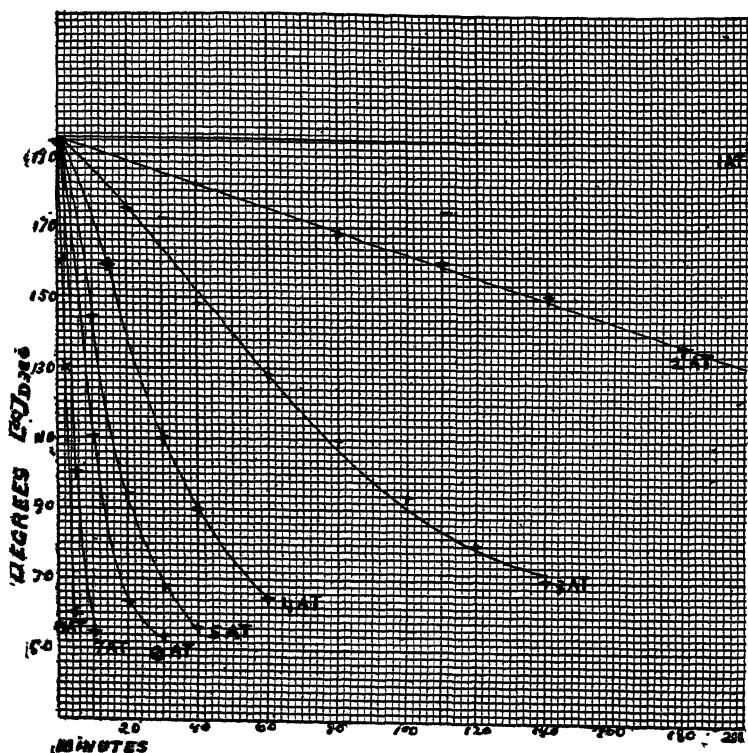
PLATE E

INFLUENCE OF TEMPERATURE, $\frac{N}{100}$ HCl.
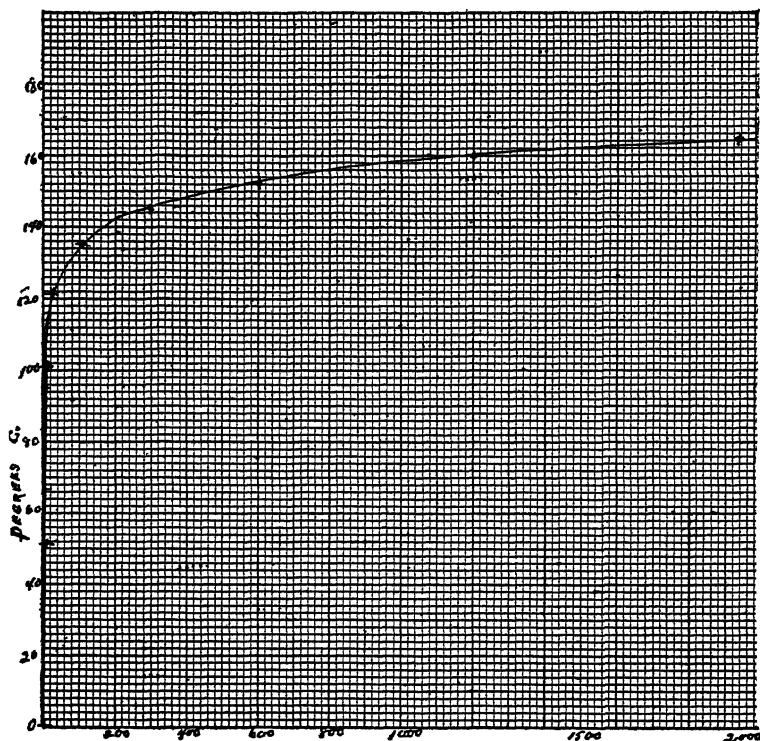
PLATE F.

INFLUENCE OF TEMPERATURE ON RELATIVE SPEEDS OF HYDROLYSIS. $\frac{N}{100}$ HCl AT 134°c [3AT]=100.

Details of values and calculations have been omitted, as reference has been made[1] to an earlier article dealing with this problem, but it was felt necessary to include some of the former results in this paper as they had a bearing on the work in hand   The original work has been extended to include values obtained at lower as well as at higher temperatures, and it is now given as a whole.

Relative speeds of hydrolysis have been recalculated to a basis referred to that $\frac{N}{100}$ of HCl at 134°=100.

The summary of results is given in the following tables:

Table I shows the influence of the various acids on the speed of hydrolysis at the same temperatures, in this case 134° C. See also Plate C.

Table II gives the influence of varying amounts of acids, at 145° C. See plate D.

Table III shows the influence of different temperatures, the amount of acid being constant. See Plate 6. The relative effects of temperature change are shown graphically in Plate F.

TABLE I

Acid	Concentration	Average c_1	Relative speeds $\frac{N}{100}$ HCl at $134 = 100$
Hydrochloric	0.02 N	0.0234	200.
Sulphuric	0.02 N	0.0118	100.7
Oxalic	0.02 N	0.0048	40.8
Sulphurous	0.02 N	0.0011	4.8
Acetic	0.02 N	0.0002	.8

TABLE II

Acid	Concentration	Average c_2	Relative speeds $\frac{N}{100}$ HCl $= 100$
Hydrochloric	0.005 N	0.0155	33.1
Hydrochloric	0.01 N	0.0314	67.0
Hydrochloric	0.02 N	0.0678	144.7
Hydrochloric	0.04 N	0.1413	301.4

TABLE III

Acid	Concentration	Pressure Atmospheres	Temp. °C.	Average c_1	Relative speeds $\frac{N}{100}$ HCl at 134°C. $= 100$
Hydrochloric	0.01 N		0°		
Hydrochloric	0.01 N		50°	0.00001	.1
Hydrochloric	0.01 N	1	100°	0.0003	2.5
Hydrochloric	0.01 N	2	121°	0.0028	22.8
Hydrochloric	0.01 N	3	134°	0.0120	100.
Hydrochloric	0.01 N	4	144°	0.0323	278.
Hydrochloric	0.01 N	5	152°	0.0668	570.
Hydrochloric	0.01 N	6	159°	0.0976	1171.2
Hydrochloric	0.01 N	7	165°	0.1582	1898.4
Hydrochloric	0.01 N	8	171°	0.2240	2688.

It was found that starch paste would hydrolyze with acids even at zero C. but the rate was too slow to measure with the polariscope, although the hydrolysis could be followed by Fehling's solution. At this temperature the action was extremely slow in comparison with that obtained at higher temperatures.

The starch molecule evidently becomes very "labile" at temperatures above 100° C. as is evident from the remarkable increase in the relative speed of hydrolysis with rise of temperature.

The curve in Plate F is found to have a logarithmic equation, expressed by the formula $\log r = mt - c$, which from the plot resolves to: $\log r = 0.0444\,t - 4.014$, where r is the rate of speed and t the temperature centigrade.

I am greatly indebted to Mr. George W. Rolfe for much assistance and kindly criticism in this work.

SOME SPECIAL ASPECTS OF STARCH

By Chester B. Duryea
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Natural or ordinary starch granules should be said to be or to constitute starch itself. Thus basically this substance is definable as the systems of essentially carbohydrate material comprising normal starch granules.

As an indication of the extent of variation in properties between various kinds of normal starches as naturally occurring with granules diverse in size, I cite a result from an investigation carried out by me about four years ago. Aqueous suspensions of potato and maize starches were acidified with hydrochloric acid and maintained at 45° C., at a gravity of 14° Bé, for considerable periods of time. Samples were systematically taken and examined. Acidities during treatments were 1.2 and 0.6 per cent HCl for the potato and maize starches, respectively.

The potential viscosity of the potato starch, at the outset, was of course far greater than that of the maize; so much so, indeed, that it was impracticable at the time to make a direct comparison that was satisfactory. Viscosimetric determinations on a uniform basis of concentration, conducted so as to follow the course of the hydrolysis, or modification, showed that for the same reduced viscosity in each case just coming within the range of the method used the potato starch required about four hours' treatment, as against one hour for the maize, although the former starch had been acted upon by an acidity twice as great as the latter. A useful system of intercomparison of starches could be developed along these lines, taking cognizance also of significant differences in modification curves, and it would be all the better for a correlation with it of the cupric-reducing powers of the washed granules, etc.

As regards new physico-chemical evidence respecting a heterogeneous structure of starch granules and of the quality of the structure, the following outline is offered.

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I have found that acid hydrolyzed or modified starch granule products of the same general viscosity, produced in the one case by what I have termed the "in-suspension" process and in the other by the older "drying-in" method, react differently during their hydrolysis, and when finished show differences in their properties. For products carried well along in modification, in part these differences may be summarized, thus:

1. By the "drying-in" process a markedly greater percentage of the substance of the granules becomes soluble, although the general type of water soluble products remains much the same, as indicated by ratios of cupric reducing to apparent specific rotation values.

2. Of the two varieties of thoroughly washed products, that yielded by the "drying-in" process possesses much the greater specific reducing power.

Herein I can only suggest my explanation, which is indicated by the statement that I believe the differences between the "drying-in" and "in-suspension" results tend to prove a non-homogeneous, or selective, concentration of water and acid within the granules, wherein their substance is less compact and more hygroscopic, during the progress of the former process—thus because of inherent variations in the granule substance developing a differentiation from normal "in-suspension" conditions.

To a considerable extent, I have obtained evidence of a similar nature through comparisons of results from "in-suspension" treatments at 55° C., the normal incipient swelling point of maize starch granules, and treatments at 59° C., at which temperature there is material general swelling. This seems to take place in such a way as to relatively increase the condition of hydration, and so the hydrolytic susceptibility, in the very same parts of the granules within which water and acid appear to concentrate during "drying-in" procedure.

As regards the amylopectin hypothesis abandoned by its authors as untenable, but revived by Matthews and Lott in a greatly modified form (J. Inst. Brewing, 1911, pp. 219–270), it does not seem to me just to argue so exclusively from evidence secured in the main from diastatic or other reactions with starch pastes, however valid by themselves such evidences may appear

to be, for the reason that the matter primarily relates to the composition of starch granules.

Citing and discussing in this connection a single instance familiar to all, some work done by Brown and Morris (J. Chem. Soc., 1889, 449), in the course of which potato starch granules were treated in the cold with moderately dilute mineral acid, seems to bear upon the amylopectin idea. At the end of $8\frac{1}{2}$ years, these distinguished investigators found about 40% of the original granules appearing in solution as glucose, while the residual 60% remained in the form of granule débris, having the composition and properties of Nägeli's amylodextrin. My own general experience is to the effect that the more resistant portions of at least maize starch granules contribute very importantly to characteristic starch viscosimetric phenomena and to the production of primary maltose, and further that under suitable conditions of paste preparation these portions all yield the characteristic blue iodine reaction. This, as I understand the question, is contrary to the amylopectin theory, but is supported, I believe, by the work of Brown and Morris cited. It would certainly seem, in their experiment, as if the more easily attacked portions of the granules naturally must have been those which were converted into glucose, while the more resistant were represented by the residue. In view of the fact that the equivalent of the 40% of original carbohydrate in solution was all glucose, and of the circumstance that the 60% as residue was a single substance, all readily converted into maltose by diastase, and so easily carried into glucose, a conclusion appears manifest that, so far as the granules were concerned, the main differences between the various parts of their substance, and between the granules of different size, were those affecting solubility, and further that owing to the long time of treatment action had become so slow that the rate of conversion into glucose, of the matter dissolved, was greater than the rate of solution of the granules. The solid matter had also reached an equilibrium state of a single well defined substance, which because of its properties might well be said to be the lowest member of a simplifying series of true starchy dextrins, and which as already stated was entirely converted by diastatic digestion into maltose—readily in turn transformed to

glucose, the sole carbohydrate found in the solution. To complete a train of ideas strongly in favor of a belief in a general chemical unity of the original granules, at this point attention should be invited to the further related fact that among the soluble products resulting from the acid hydrolysis of starch granules not glucose but maltose is the sugar first formed (J. Soc. Chem. Ind., 1911, 30, 789), and that this chemical individual continues to be the characteristic or constitutional sugar product for a very considerable portion of the hydrolytic course. In my own work with normally mixed maize starch granules modified by the "drying-in" process, I have traced this last mentioned condition as obtaining to a point where 9.0% of the original granules had become soluble. At this stage the combined water extracted products had the constants $[a]_D^{20} = 192.4°$ and $R = 14$, both values being references back to an original anhydrous starch equivalent of the carbohydrates in solution. The phenylhydrazine acetate test on the mixed products yielded abundant maltosazone, but gave entirely negative results for glucose.

So much space has been given over to sketching aspects of starch as starch, that is, as starch granules, that the remainder of this paper must be very brief.

I would, however, like to confirm recent evidence (Fernbach and Schön, J. Soc. Chem. Ind., 1912, 402) to the effect that "there is no reason to consider that the acid saccharification of starch proceeds differently from the diastatic, at least, during its earlier stages", by the statement that I have found through extended experience with normal and modified maize starch granule pastes, under conditions of very low acidity and high concentration (as high as 36%), that, up to a stage short of the formation of any considerable relative amount of glucose, there is apparently no profound divergence in normal acid hydrolysis from the general results characteristic of physiological or enzymic digestion.

Pastes other than aqueous, such as pastes with solutions of alkalies, chloral hydrate, various deliquescent salts, etc., have been considered to be outside of the scope of this paper.

With regard to the synthesis basic to starch formation, we all know that protoplasm, chlorophyll, light and carbon dioxide are involved. After starch is once formed, translocations with re-

deposition of granules take place without intervention of chlorophyll and light.

In this connection, I would suggest the idea of a special biological condition or field, dynamically actuated by electro-magnetic light. Applied to the starch manufacturing chlorophyll cells of plant leaves, my thought may be outlined as follows:

1. Because of the colloidal and stable character of the chloroplasts, the condition of existence of water therein, and the general and specific properties of carbon dioxide in relation thereto, when molecules of this gas are first taken up from the atmosphere they may be to an extent somewhat loosely held rather than firmly bonded chemically.

2. The conditions of absorption of the CO_2 molecules, by the colloidal chloroplasts, enormously reduces the rate and amplitude of their general motions even as compared with solution in water, and brings them within the range or sphere of the specific influence of the wave fronts of light.

3. These circumstances introduce the carbon dioxide complexes under conditions of existence within a reacting system of chloroplasts and light, in such wise that they may become caught by or engaged with this specific mechanism of active fluorescence, and thus become unstable. Decomposition would ensue, accompanied by the formation of new carbon compounds. The carbohydrate type of these new bodies might be facilitated if the light action also aided in depolymerizing some of the water present.

This idea of special colloidal fields, I believe, may apply very generally to vital processes, as providing for a more intimate and specific relationship between molecules than exists in the ordinary states of solutions.

With regard to a general bio-chemical formula for starch, it seems to me that no evidence may be valid except it is secured under circumstances which are compatible with the conditions of starch synthesis, and consistent also with the known conditions and facts connected with the reversibility of biological translocations of this substance. Of the formulas proposed, it therefore still seems best to prefer for the present that advanced by A. R. Ling, in 1909 (VIIth Internat. Congress App. Chem., Sec. VI B, p. 123), which in a little different form may be written $(C_6H_{12}O_6)_n - (H_2\Theta)_{n-1}$.

SUR UNE NOUVELLE FORME D'AMIDON SOLUBLE

Par M. A. Fernbach
Professeur à l'Institut Pasteur de Paris

(Note préliminaire)

M. G. Malfitano et Melle Moschkoff ont montré récemment (*Comptes rendus de l'Académie des Sciences,* 12 février 1912) que de l'amidon déminéralisé, préparé par leur méthode de congélations successives, se dextrinise en devenant peu à peu soluble lorsqu'on le soumet à la dessiccation, c'est à dire par déshydration. Ce résultat nous a suggéré l'idée de transformer de l'amidon en sa forme soluble par l'action de déshydratants, parmi lesquels nous avons essayé tout d'abord l'alcool absolu et l'acétone pure. Nous nous bornons à mentionner dans la présente note les résultats obtenus avec l'acétone, sur laquelle ont surtout porté nos expériences.

Si on verse dans un grand excès d'acétone pure de l'emplois d'amidon à 1 ou 2%, préparé avec de la fécule de pommes de terre du commerce, c'est à dire n'ayant subi aucun traitement préalable pour sa déminéralisation, on obtient un précipité floconneux, qui se forme au fur et à mesure que l'empois tombe en mince filet dans l'acétone fortement agitée.

Le précipité, recueilli sur un entonnoir de Buchner, est broyé dans un mortier avec de l'acétone pure, essoré et séché dans le vide sec. On obtient ainsi une masse parfaitement blanche, pulvérulente et très légère, qui présente cette particularité très intéressante d'être soluble, non seulement dans l'eau chaude, mais aussi *dans l'eau froide.* Deux grammes de cet amidon soluble se dissolvent facilement à froid dans 200 centimètres cubes d'eau, en ne laissant comme résidu insoluble qu'une fraction infime de la masse primitive.

L'amidon soluble obtenu par la méthode que nous venons de décrire présente sur les amidons solubles préparés par les procédés indiqués jusqu'ici l'avantage appréciable d'être totalement

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dépourvu de pouvoir réducteur.   Il se saccharifie facilement par
l'extrait de malt, exactement comme l'empois d'amidon qui a
servi à le préparer.   Sa solution, qui filtre facilement sur du papier,
se colore par l'iode en bleu pur intense.

⊦ L'obtention d'un amidon presque intégralement soluble à froid
exige qu'on emploie pour sa préparation un empois dilué.   Si on
dépasse pour cet empois la concentration de 2%, on obtient un
produit qui n'est que partiellement soluble à froid; on peut séparer
la portion soluble par filtration sur du papier, bien que cette filtra-
tion soit très lente, et ce qui reste sur le filtre a un aspect tout à
fait comparable à celui de l'empois d'amidon.

Nous avons constaté que si on précipite par l'acétone ou par
l'alcool une solution préparée à chaud d'amidon soluble obtenu par
la méthode de Fernbach-Wolff (*Comptes rendus de l'Académie des
Sciences*, 15 Mai 1905), lequel est absolument insoluble à froid, on
obtient, à la suite d'une agitation énergique, un précipité floccon-
neux, qu'on arrive à séparer par centrifugation, et qui, après
séchage dans le vide sec, se dissout intégralement dans l'eau froide,
mais en donnant une solution moins limpide que l'amidon soluble
obtenu par précipitation d'un empois dilué au moyen de l'acétone.

Les solutions de la nouvelle forme d'amidon, soluble à froid,
présentent, comme l'empois qui a servi à le préparer, la propriété
de subir le phénomène de la rétrogradation.

Les recherches brièvement exposées dans ce qui précède ont été
exécutées avec l'aide de M. M. Schoen, auquel nous exprimons
ici tous nos remerciements pour son concours précieux.

THE CHEMISTRY OF STARCH

By G. B. FRANKFORTER

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Starch is the most important member of the group of organic compounds commonly known as the carbohydrates. It is not as abundant as its sister compound, cellulose, but the *rôle* which it plays in both plant and animal life easily places it in the front rank. It has been known to the human race for centuries. The early history of the science of chemistry shows that those substances which exist free in nature, or those substances which are easily prepared, were the first to be studied and used. Starch is easily prepared from the various cereals and very easily from tubers, like the potato Starch was doubtless first prepared from wheat grown in Mesopotamia, in Palestine and in Egypt. Dioscorides about the middle of the first century of the Christian Era gives the first account of its preparation from wheat. From his meagre descriptions of this, and other early industrial chemical and mechanical processes, and from the fact that many of these processes doubtless required some special chemical knowledge and mechanical skill, one may, I think, conclude that some of these processes must have developed very slowly and that starch and possibly sugar must have been prepared centuries before the Christian Era. It is evident, however, that neither starch nor sugar could have been prepared in large quantities, for both during the early centuries were regarded as luxuries.

From what has been handed down concerning the early preparation of starch, there seems to be little doubt but what it was obtained in much the same way as it is prepared today, the chief difference apparently being that the machinery used for each succeeding generation has improved, so that it could be prepared in purer form and in larger quantities. At any rate, starch has long since changed from the luxury class to the most important of all of the foodstuffs.

Starch is widely distributed in both the plant and the animal world. It occurs in all plants in greater or less quantities, for it

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seems to be formed whenever chlorophyl is exposed to sunlight. Bulkewitsch (Biochem. Centr. 10-314) found that starch was the first carbohydrate formed in *Morus alba* and *Saphora japonica*. He does not, however, state that it was formed through the action of chlorophyl, but quite the contrary. He found that twigs of the above species when kept at room temperature for some time produced starch, and attributes its formation to enzymes, starch, however, being the first carbohydrate formed. While this and other experiments along the same line are important, the evidence at present is certainly not sufficient to prove that in all cases starch is the first carbohydrate formed in plant growth. Incidentally, it was shown by Bulkewitsch that while starch is formed by enzymic action, there are either several varieties of enzymes or the same become inactive under different conditions.

Another interesting reaction is the change produced by hydrogen peroxide (Comp. rend. 148-578). Common starch, glycogen and inulin undergo both hydrolysis and oxidation in the presence of small quantities of hydrogen peroxide. Whether the small quantity of hydrogen peroxide in the air plays a part in the chemistry of the starches and sugars is certainly a problem worthy of careful experimentation. Starch is present in plant growth from the time the seed begins to germinate until the plant has reached maturity. It is in all seeds and especially in the cereals, where it is stored up for the purpose of supplying the young plant with food until it is large enough to produce its own supply.

But starch is by no means confined to the plant world. Its importance in the animal world is now a matter of common knowledge although the chemical processes involved in its formation are by no means clear. In a modified form, commonly known as glycogen, it doubtless plays much the same part in the physiological chemical processes that common starch does in plant growth if all its functions were known. It appears to be formed from common starch by enzymic action.

Physical Properties. Starch from any one of the great sources when pure is of a very light creamy white color with no odor and no taste. Its specific gravity is given as 1.505, although under certain conditions it may be as high as 1.59. Potato starch turns red litmus paper blue, according to some authors, but as a general

rule the reaction is neutral. While starch from the various species of plant seem to have the same general properties, it requires but a glance to show that almost every family of plants has its own peculiar form of starch granules. The difference is entirely physical and doubtless means simply different aggregation of molecules which go to make up the granules themselves. Thus while wheat and corn starches apparently have the same molecular form and structure, these molecular aggregations or granules are so different in size and shape when examined under the microscope and especially in polarized light, that the chemist familiar with these different forms finds no difficulty whatever in identifying the source of any of the common forms.

The Chemistry Proper of Starch. The development of starch chemistry has been very slow, taking into consideration its importance and the vital part which it plays both in plant and animal life. Probably no other great important organic compound, not even excepting its complex sister compound, cellulose, has been so little studied from the purely chemical point of view as starch. A casual glance into the history of organic chemistry and especially that branch known as phytochemistry, reveals the fact that with few exceptions the mass of chemical work has been confined to compounds which have distinct crystalline forms, or else admit of purification by some more or less simple process. This is doubtless one of the reasons why the complex compounds like the alkaloids began to be studied nearly a century earlier than the common and more important substances like the sugars, starches and celluloses. During the last quarter of a century hundreds of chemists have worked more or less closely with the carbohydrates, but Kiliani, Tollens, Emil Fischer, Cross and Bevan and perhaps half a dozen other investigators would include practically all the men who really succeeded in obtaining from this most important group of compounds distinctly positive results. As a matter of fact, the molecular constitution of the starches and the resins have, up to the present time, seriously occupied the attention of but a very few, most chemists regarding them as too complex for serious consideration. The wonderful work of Fischer, Tollens, Wohl and others on the sugars, however, leads one to believe that in the not very distant future the constitution of all of

the common sugars as well as starch and cellulose will have been worked out, and the molecules built up from simple forms like formaldehyde and its polymerized derivatives, the simple hexoses.

The first really important chemical work on starch which I have been able to record was done by Kirchhoff in 1811 (Schweigger's Journal, 4-108). Kirchhoff showed that when starch is heated with dilute acids it dissolved, and on removing the acid and the water the substance remaining was no longer starch, but a mixture of several substances belonging to the sugar group, among them the well-known substances dextrine and dextrose. A few years later the same investigator showed that similar substances were formed when starch was subjected to certain forms of fermentation which, from his description, must have been identical with modern diastatic action. These, like many important chemical reactions, were not regarded as important at the time of their discovery. It was more than a half century after Kirchhoff's observations that the importance of his discovery was fully appreciated and made use of commercially. The breaking up of the starch molecule by boiling water is another phenomenon which until recently was practically unknown, although it must have been observed for several generations.

What happens molecularly in these hydrolytic reactions is largely a matter of speculation, for while various more or less conventional equations may represent what changes take place, it is obvious that only the most general equation will indicate what changes really occur when starch is hydrolyzed either by boiling water or by acids. In the former case dextrine is largely formed, while in the latter the final product is dextrose. Assuming that the reaction is complete, it may be represented by the following:

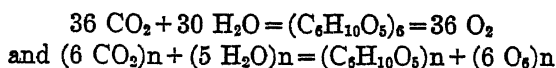$$(C_6H_{10}O_5)_6 + 6\ H_2O = 6\ C_6H_{12}O_6.$$
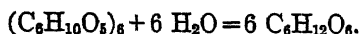
The above formula for starch is based on early investigations especially of starch iodide. The size of the starch molecule evidently cannot be determined with accuracy from the iodide, as different investigators have obtained results varying from $(C_6H_{10}O_5)_2$ to $(C_6H_{10}O_5)n$ when n is greater than 6. From th writer's experience and the results obtained by several investi gators, the hexapolymer seems to have a slight preference over
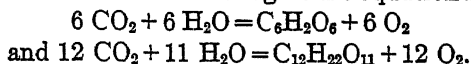
either $(C_6H_{10}O_5)_2$ $(C_6H_{10}O_5)_4$ and $(C_6H_{10}O_5)_6$. It must be remembered as pointed out by Ling (Seventh Int. Cong. of App. Chem., London, 1909), that these and the formulæ presented in this paper are only attempts to formulate some of the chemical facts concerning starch.

Synthesis of the Starch Molecule. A. W. v. Hofmann, I think, was the first to show that formaldehyde played an important *role* in the building up of the complex phytochemical compounds like sugar, starch and cellulose. Difficulties arose in his attempt to explain the synthetic action because, while he assumed formaldehyde to come from carbon dioxide, he regarded it as existing only in the hydrated form, which somewhat complicated the common polymerization theory. Hofmann also failed to prepare formaldehyde directly from carbon dioxide. Since Hofmann's time, however, formaldehyde has been prepared by the action of sunlight on carbon dioxide (Trans. Chem. Soc. 1907-91-687). Thus when carbon dioxide is passed into water in which has been placed metallic magnesium, some of the gas is reduced to formaldehyde. For conversion of formaldehyde into the sugar group, see Loew's and Butlerow's works on formose and methylenitan. Baeyer (Ber. 3-67) went farther and laid the first solid foundation upon which the carbohydrate synthesis might be built, by giving very general exposition of what takes place in the formation of the carbohydrates, especially starch and cellulose in the following equations:

$6\ CO_2 + 5\ H_2O = C_6H_{10}O_5 + 6\ O_2$. This equation may be enlarged so as to indicate the complexity of starch or cellulose by the following:

$$36\ CO_2 + 30\ H_2O = (C_6H_{10}O_5)_6 = 36\ O_2$$
and $(6\ CO_2)n + (5\ H_2O)n = (C_6H_{10}O_5)n + (6\ O_6)n$
Or in the case of the sugars the equation may be as follows:
$$6\ CO_2 + 6\ H_2O = C_6H_2O_6 + 6\ O_2$$
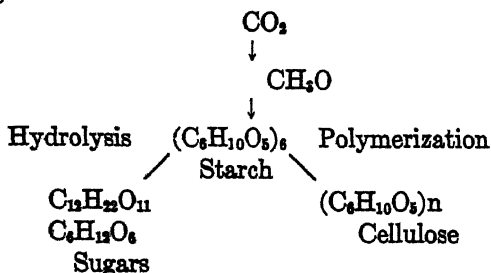and $12\ CO_2 + 11\ H_2O = C_{12}H_{22}O_{11} + 12\ O_2$.

What these equations represent even at the present time is simply that certain chemical changes take place and that certain compounds are formed. They are not presumed to explain either the intermolecular changes which take place or the direction in which the reaction always proceeds. Considerable data has been

already obtained, but not sufficient to determine with accuracy the direction of the reaction in all cases.

Logically followed out, one would assume that synthetic reactions always proceed from the simple to the more complex, in which case formaldehyde would pass to polymers if two, three and six molecules, as for example, para formaldehyde, trioxymethylene and the hexoses, as formose and methylenitan. Then, again, by a dihexa and a polyhexa-polymerization it changes to the disaccharides and finally to the starch and cellulose groups. However vague these assumptions may seem, they do represent from the purely logical point of view, the most plausible explanations of facts concerning these important compounds.

Facts, however, do not in all cases bear out the theory. The fact that starch is the first carbohydrate to appear in the leaves of plants by action of light on chlorophyl is difficult to reconcile to the progressive theory given above. Payen (Compt. rend. 53-813) showed beyond a doubt that not only green fruit but also the plants themselves, including the leaves, contain an appreciable amount of starch. Starch would seem to be, at least in certain plants, the first carbohydrate formed, so that in the formation of cellulose and grape sugar there is further polymerization on the one hand and hydrolization on the other, as indicated by the following diagram:

$$CO_2$$
$$\downarrow$$
$$CH_2O$$
$$\downarrow$$

Hydrolysis $(C_6H_{10}O_5)_6$ Polymerization

Starch

$C_{12}H_{22}O_{11}$ $(C_6H_{10}O_5)n$
$C_6H_{12}O_6$ Cellulose
Sugars

That experimental evidence at the present time is too meagre to attempt even to trace the details of the changes which take place in the formation of starch, is self-evident. Baeyer's theory in general seems to come nearer to the facts than any other thus far presented. Some phytochemists, however, are inclined to modify the theory, holding as indicated above that not only all carbo-

hydrates but all compounds, like the resins, gums, essential oils and terpenes, are direct derivatives of starch.

If these phytochemical facts are accepted as having a bearing on the starch molecule, they would tend to give starch a complex ring structure, as most of these substances as the resins, the gums, the terpenes and essential oils are ring compounds beyond a doubt. Following out this line of reasoning, Kronstein represented the resins which he regarded as direct derivatives of starch as ring compounds. If the starch molecules were constructed from Kronstein structural formula for the resins, the generally accepted starch molecule $(C_6H_{10}O_5)_6$ would have the following formula, in which each group or starch unit is joined to its neighbors as explained in the aldehyde polymerization.

$$C_6H_{10}O_5$$

$$C_6H_{10}O_5 \qquad\qquad C_6H_{10}O_5$$

$$C_6H_{10}O_5 \qquad\qquad C_6H_{10}O_5$$

$$C_6H_{10}O_5$$
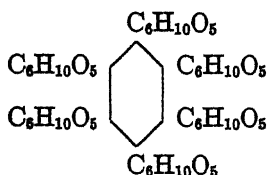
Cross and Bevan (Ber. 42-2198) in their application of Traube's theory of the relationship between the molecular volume and molecular solution volumes of compounds and their molecular weights, found that the molecular solution volumes of both starch and cellulose are lower than calculated by Traube (Ann. 290-43). They suggested that the low numbers were probably due to certain molecular arrangement, possibly to ring structure. Traube, himself, was requested by the authors to present his views on the subject and in a short review of the work suggested that the only way to explain the discrepancies was by the ring theory.

It does not follow from the above statement that the ring compound is used in the same sense that it is when applied to the aromatic compounds which are characterized by their great stability. It is more likely to be a polymerized form of the aldehydes which may be represented by a ring form.

The only other evidence which I have found concerning the ring form for starch is the fact that the resins are ring compounds
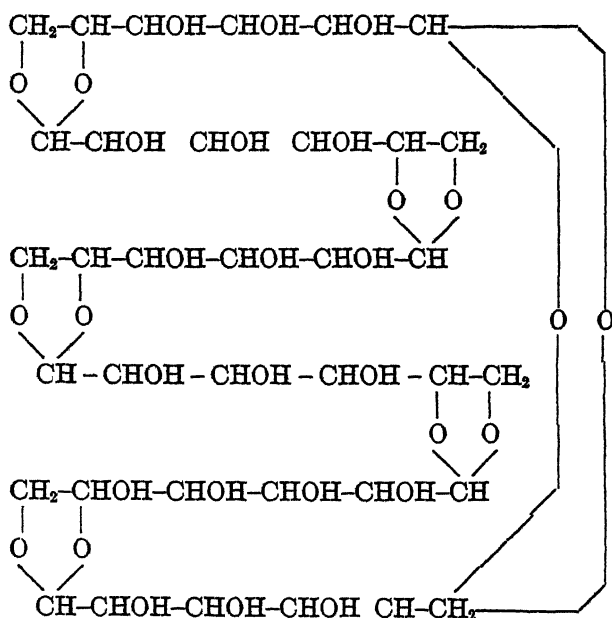
and the resins have been assumed to be direct derivatives of starch. The writer's work on the resins, however, indicates that the resins come from the terpenes rather than from starch, therefore to assume that the complex resin molecules come from starch is to assume that the terpenes themselves are produced from starch. The change of the starch molecule into a ring compound and its oxidation into the resin acids would be such an unusual chemical change as to require a large amount of experimental evidence to verify it.

The synthesis of the starch molecule it would seem to me should come from the sugars proper, although the appearance of starch as one of the first of the common substances formed in plant growth is rather an important evidence and favors starch formation without passing through the simpler sugar groups. Be the synthesis as it may, the relationship between the sugar and the starch molecules is very close, no matter whether the reaction proceeds from the simpler to the more complex or *vice versa* in plant growth.

From Fischer's work on the sugars and his structural formulæ for some of the disaccharides, it seems more probable that a reaction similar to the condensation of the mono to the disaccharides and the condensation of the di to the polysaccharides, comes nearer representing what actually takes place in plant growth than the starch and especially the starch ring theory. Thus a disaccharide may be represented as derived from the monosaccharides by the following condensation:

$$CH_2OH \; CHOH-CH-CHOH-CHOH-CH. \; .O-CH_2 \; (CHOH)_4 \; CHO$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{O}$$

By continuing these condensations, compounds of two, three or more of the mono or hexahexose molecules may be formed, as for example, $C_{12}H_{22}O_{11}$, $C_{12}H_{32}O_{10}$, $C_{24}H_{42}O_{21}$ and $C_{36}H_{62}O_{31}$ or $C_{36}H_{60}O_{30}$. By following out the Fischer condensation idea, a starch molecule of any size may be built up. Even Geinsberghens molecule for cellulose $(C_6H_{10}O_5)_{34}$ lies quite within the reaction limit.

Wacker (Ber. 41-266) has succeeded in determining the complexity of the starch molecule in terms of the hexose groups. The method employed depends upon the fact that p. phenylhydrazine sulphonic acid and other hydrazines produce with aldehydes and alcohols by the aliphatic series, in the presence of excess of alkalies, an intense red color. The dye formed varies very little with the different carbohydrates, at least not sufficiently to interfere with the use of the method. He formulated the following law that the color intensity decreases with increase in molecular weight. By working out some thirty or forty different compounds, he obtained data such as would enable him to determine the molecular weight of the complex as well as the simple carbohydrates.

Later (Ber. 42-2675) he extended his experiments to starch. He found the number of hexose groups to vary from 5 to 8, giving for the less soluble granulose the mean, or six groups in the molecule. Glycogen, although it has generally been accepted as having a smaller molecule than common starch, was found to vary, but on the whole he found it to be more complex, the number of groups being approximately 10.

The following is a table of the different forms of common starch:

Very soluble starch... . ...5 hexose groups

Difficultly soluble.............................6 hexose groups

Once dissolved................................7 hexose groups

Several times dissolved.......................8 hexose groups

The fact that dextrine contains the aldehyde groups (Ber. 23-3060) indicates that the aldehyde groups are no longer neutralized by polymerisation, but have been liberated by hydrolysis on the one hand, and perhaps a splitting off of a part of the starch molecule on the other, dextrine being first, and dextrose finally formed by complete hydrolysis. Thus if starch is represented by condensed hexahexoses, by following out Fischer and Ladenburg, the molecule may be represented by the following:

CH₂-CH-CHOH-CHOH-CHOH-CH————

The structural chemistry diagram shows:

$$CH_2-CH-CHOH-CHOH-CHOH-CH$$

CH-CHOH CHOH CHOH-CH-CH₂

CH₂-CH-CHOH-CHOH-CHOH-CH

CH - CHOH - CHOH - CHOH - CH-CH₂

CH₂-CHOH-CHOH-CHOH-CHOH-CH

CH-CHOH-CHOH-CHOH CH-CH₂————

It must not be construed that these formulæ mean anything more than an attempt to apply certain known facts to the starch molecule. Apparently, the starch molecule is at least of the above size, probably greater than the hexa form. It contains no aldehyde groups, but by hydrolizing it is readily converted into dextrine, which may be represented by breaking one of the hexa groups and the taking on of a molecule of water to form an aldehyde. At any rate, it probably comes nearer to the general structure of the starch molecule than the old generally accepted formula $(C_6H_{10}O_5)n$.

Glycogen. The chemistry of starch would not be complete without at least a brief *résumé* of some of the modified forms of starch, as glycogen and inulin. Common starch, as the term is ordinarily understood, seems to be produced in the plant world only, but as there are many different sugars, so there are doubtless many different starches. The starch which occurs most abundantly in the animal world is known as glycogen or animal starch. Glycogen occurs in both the herbivorous and carnivorous animals, especially

in the liver and heart.   Its origin is not entirely clear, although there seems to be little doubt but what it is formed largely from common vegetable starch notwithstanding the fact that it appears quite as abundant in the carnivorous as it does in the herbivorous animals.   Its composition is still unsettled, but from its combination with barium hydroxide, forming a well characterized compound $(C_6H_{10}O_5)_5$ Ba $(OH)_2$, (Arch. f. d. ges. Physiol. 37-582), the molecule appears smaller than the common starch molecule, the result of either a partial breaking down of common starch through metabolistic changes or through partial hydrolysis.   Glycogen is readily prepared from the liver by treating the organ with hot water and allowing to stand for some time, then filtering and precipitating out the glycogen with alcohol.

Glycogen in some respects resembles common starch, while in others it differs widely.   It is soluble in water, thereby differing from common starch.   It has about the same specific gravity. In solution it is optically active, turning the plane of polarization strongly to right, $(a)_D + 200°$ or nearly four times more active than dextrose.   Its identification and separation from common starch are due to the fact that it dissolves in water with a peculiar opalescence, while starch is insoluble and naturally does not produce the opalescence.   It differs from starch in its·reducing power after having been hydrolized by acids and from the fact that it is converted by ferments directly into dextrose.   It forms with iodine, in the presence of sodium chloride, a reddish brown solution, and with benzoyl, chloride and sodium hydroxide a well characterized, while powdered benzoyl glycogen (Zeit. f. Physiol. Chem. 13-125).   Treated with potassium hydroxide it is slowly decomposed.   With common mineral acids it reacts not unlike starch, changing to dextrine, then to maltose and finally to dextrose.   A similar change takes place by diastatic or pancreatic action.

As has already been stated, the chemical changes which take place in the formation of glycogen are by no means clear.   That the change of whatever nature is complex and deep-seated, probably involving a series of unidentified substances with the general characteristics of starch, is evident from the experiments of various writers.   Thus Naegeli (J. 1859-544) has shown that in the chang of common starch to glycogen, several compounds mostly unidenti

fied are formed in the intermediate stages between common starch and glycogen.

Daresto (Compt. rend. 72-845) found that the yolk of freshly layed eggs contains a substance with the granular appearance and with many of the characteristics of common starch, being optically active and giving the blue starch iodide reaction in the presence of iodine. A study of eggs after incubation indicates that three and perhaps four compounds are formed in the change of starch to dextrose. In fact, Daresto found during the stage of incubation that there were successive changes from starch to dextrose, and *vice versa*, so that the common reaction given for the change of starch to dextrose may be made reversible and as follows:

$$C_6H_{10}O_5 + H_2O \leftrightharpoons C_6H_{12}O_6$$

The writer has verified many of these experiments and therefore believes that there is at least one intermediate substance of starchy nature between starch and glycogen.

Schutsenberger (Ann. Chem. Pharm. 140-74) has shown that acetic anhydride not only combines with starch to form a well characterized triacetyl derivative but also with glycogen, forming a somewhat similar triacetyl compound. These acetyl compounds are very important in the identification of the respective starches. The writer believes that the acetyl and benzoyl derivatives will prove to be of more importance in the working out of the constitution of the starches than any other reactions known at the present time.

Inulin. Inulin, another form of starch, is distributed through a large group of plants in which it evidently plays the part of common starch. It is readily obtained by digesting the material containing the inulin with hot water. It is again precipitated on cooling. It resembles starch very closely in its general physical properties, but in its chemical properties it differs widely. While it seems to take the place of starch in certain cases, its function must be different, inasmuch as it exists in plants in the form of a solution, which necessitates different functions. In the solid form it is very hygroscopic, taking on water more rapidly than starch under the same conditions. It is slightly soluble in cold water

but quite readily in hot, from which it separates out on cooling in the form of a powder. Heated with water or dilute acids, it changes to lævulose. It is colored brown by iodine, thus resembling glycogen. It is a powerful reducing agent, readily precipitating copper and silver from their salts. Little is known of its constitution, but according to the work of Tanret (Compt. rend. 116-514 and Bul. soc. chim. 9-227) who has studied several of the starchy compounds including inulin, pseudo inulin and inulenin, the size of the inulin molecule is the same as the formula given for common starch, namely $(C_6H_{11}O_5)_6 \cdot H_2O$ or $C_{36}H_{62}O_{31}$, notwithstanding that a molecular weight determination by the Raoult method gave numbers which agreed with penta instead of the hexa polymer.

In conclusion, it should be stated that some of the important references have been omitted because they have been referred to in a general *résumé* of starch chemistry in the proceedings of the previous congresses. The whole paper, therefore, had to be modified on this account.

The writer desires to state in conclusion that he believes starch offers more opportunities to the chemist for important discoveries than any other group of compounds in the whole realm of organic chemistry. Not only is the chemistry proper of vital importance as offering an almost boundless field, but also the great vital subject of fermentation which is so closely connected with the starch. It is to be hoped that in the near future chemists may give more of their time to the chemistry of starch and especially fermentation. If chemists or botanists with a thorough knowledge of chemistry should devote more of their time to the study of starch, the next decade would see the chemistry of starch completely rewritten.

HYDROLYSIS OF CELLULOSE AND LIGNO CELLULOSE

By F. E. Gallagher and I. L. Pearl

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When wood or sawdust is cooked at high pressures with dilute acids there is formed a considerable amount of fermentable sugar, mainly dextrose. Previous investigators have differed in their opinions as to the source of the sugar, some maintaining that it is formed from the cellulose and others from the lignin. The purpose of the experiments here described is to supply additional data that will contribute to the solution of the problem.

All of the cooks referred to in this paper were made on long-leaf pine sawdust screened through a 10-mesh sieve. As hydrolyzing agent 1% H_2SO_4, figured on the dry weight of the sawdust, was used. Three parts of liquor, by weight, were used for each part of sawdust. The cook was carried out in a porcelain lined covered dish suspended over water in an autoclave. A maximum pressure of 135 pounds (9 atmospheres) was maintained for thirty minutes. The total duration of the cook, including heating up and pressure relief periods, was about 70 minutes. The cooked sawdust was completely extracted by water, evaporated to about 11° Brix (1.045 Sp. gr.) and fermented. The percentages of water soluble and copper reducing materials were determined on portions of the evaporated extract.

A series of cooks was made to determine the extent to which fairly pure forms of cellulose could be converted into sugars by this procedure. The character of these experiments and the results will be clear from Table No. 1.

These results would indicate that pure cellulose can be converted into fermentable sugars. Cotton cellulose does not give as high a sugar yield as the wood celluloses under the hydrolyzing conditions used. Each of the celluloses is capable of yielding a further amount of sugars on re-cooking, and the extract from the second cook is the more fermentable. Contrary to the data of some previous investigators, the celluloses gave lower yields of soluble material and fermentable sugars than wood. The ratio of fer-

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TABLE NO. 1
SUGARS FROM PURE CELLULOSE MATERIAL

	Total Extract	Reducing Material	Fermentable Sugars	Ratio Fermentable Sugars Total Solids
1a Bleached Cotton	3.1%	1.6%	1.4%	.44
1b Bleached Cotton (Residue from 1a recooked)	4.5%	2.8%	2.5%	.55
2a Bleached Soda Wood Pulp	17.7%	16.0%	6.3%	.36
2b Bleached Soda Wood Pulp. (Residue from 2a recooked.)	7.5%	4.3%	3.8%	.51

Note. To avoid burning, cottons were cooked at 100 lbs. instead of 135 lbs. pres.

mentable sugars to the total soluble material is about the same as for extracts from wood cooks.

At ordinary temperatures, chlorine vigorously attacks the lignin portion of wood but has little effect on the cellulose portion. This is used as the basis of several analytical methods for the determination of cellulose. We have found that chlorine, when substituted for sulphuric acid in a high pressure cook with sawdust, gave a very fair yield of soluble and fermentable material, from which it might be concluded that the sugars were formed from the lignin portion of the wood. The following data, however, indicates that under the cooking conditions used the chlorine will attack pure cellulose, converting it into fermentable sugar. In these experiments, 0.2% chlorine, in the form of chlorine water, was used. The cooking method was in other respects similar to that already described.

TABLE NO. 2
CHLORINE AS HYDROLYZING AGENT

Material	Total Extract	Reducing Substances	Fermentable Sugars	Ratio Fer. Sug. Total Ext.
Sawdust	26.7	18.4		
Sulphite Wood Pulp	13.5	10.7	8.0	.59

Since the almost pure cellulose yields fermentable sugars, but in lesser amount than the ligno cellulose material, it would appear that both the cellulose and the lignin can be converted into sugar, at least with this special reagent.

The most conclusive data bearing on the question as to whether the cellulose or lignin portions of the wood yield sugar on hydrolysis is furnished by a series of experiments in which the change in the composition of the wood on cooking with acid has been determined. The cellulose in the original sawdust, in the residue from the first cook and in the residue from the re-cook, was determined by the Dean and Tower[1] modification of the Cross and Bevan method. The results of the cooks and analyses are given in Table No. 3.

If in the first cook the lignin alone had been attacked, the residue would have contained 70% of cellulose. If the cellulose alone had been attacked, the residue would have contained 41% of cellulose. After the second cook the sawdust residue was in finely divided physical condition and noticeably carbonized. A great deal of reliance cannot therefore be attached to the last cellulose determination. For similar reasons, it did not appear to be practicable to carry out cellulose determinations on the final residue.

This experiment indicates that the cellulose and the lignin go into solution, on high temperature hydrolysis, in about the same ration as they exist in the wood. Since the ratio of $\frac{\text{Fermentable sugars}}{\text{Total extract}}$ is about the same for the wood extract as for the extracts from the pure celluloses, we conclude that both the cellulose and lignin can be equally converted into dextrose. The conversion of cellulose and wood by chlorine water is also in accord with this view.

Under the conditions of high temperature hydrolysis with dilute acid, the cellulose and the lignin do not react as chemical individuals, but rather as a chemical compound, ligno cellulose.

TABLE NO. 3

EFFECT OF HYDROLYSIS ON CELLULOSE CONTENT OF WOOD

Material	Total Extract	Reducing Material	Ferment. Sugars	Ratio Fer. Sug. Total Ext.	Cellulose Before Cooking	Cellulose After Cooking
a. Sawdust (Longleaf Pine)	22.0%	19.3%	11.8%	.53	54.0%	52.0%
b. Residue from (a)	6.3%	4.7%	3.0%	.47	52.0%	42.0%
c. Residue from (b)	2.8%	1.7%	1.6%	.57		

[1] J. A. C. S. *29* 1119.

DISTILLATION OF RESINOUS WOOD BY SATURATED STEAM

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INTRODUCTION. COMMERCIAL STEAM DISTILLATION PROCESSES

The steam distillation process for obtaining the volatile oils from the wood of the longleaf pine has been the basis of a small industry since about 1903, being introduced apparently in an attempt to produce wood turpentines at temperatures lower than those used in the destructive distillation processes then in operation, and thus to obtain a product uncontaminated by the decomposition products of wood and rosin. Quite a large number of plants have been built to use either sawmill waste or lightwood, or both, but many have been abandoned, probably only 12 or 15 being in operation in 1911. The quality of the crude turpentine produced has usually been very good, but because this is the only product obtained, or because the yield of this product is often lower than that of "crude turpentines" from other processes, the plants have been successful only under especially favorable conditions.

This process seems to be very promising, however, when combined with other processes for the utilization of the steamed chips, as for instance the extraction of the chips with volatile solvents for the removal of the rosin. Conditions are also favorable for this process in cases where the material would be largely used as fuel or wasted, or is very cheap or so poor in quality that more complicated processes would not be profitable; these conditions are commonly realized in the case of that part of the waste wood of sawmills now used as fuel at the plant or burned on the rubbish pile.

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PURPOSE OF INVESTIGATION

In the fields mentioned above the steam distillation of resinous woods will undoubtedly expand and it was in the hope of promoting this expansion and thus increasing the utilization of a class of material now wasted that this investigation on the fundamentals of the process was undertaken. There has been no uniformity in commercial practice or in the opinions of the various operators and no experimental data have been published on the effects produced by the different readily controlled variables, such as steam pressure, size of chips, or rapidity of distillation. In the methods described in various patent specifications the greatest stress has been laid on the mechanical features of charging and discharging, and of distributing the steam throughout the retort, which, although of great importance in the economy of a commercial method, throw no light on other equally important factors.

There seemed to be, therefore, a profitable field for investigation in determining the relations between the conditions under which the distillation is conducted on one hand and on the other hand the amount and kind of products and the readiness with which they are obtained.

THEORETICAL CONSIDERATIONS

In the description of the experimental work and the discussion of the results it will be necessary to refer constantly to certain theoretical principles which apply to the distillation of volatile oils with steam, and in order to make the future discussions clearer, a brief presentation of these principles is given at this time.

In order to simplify the deductions the following assumptions are made in regard to the resinous material contained in the "lightwood" from the longleaf pine:[1]

[1] M. Vezes (Bull. Soc. Chem. *29*, 470-478, 1903) has given a very clear and complete discussion of the principles underlying the distillation of the oleoresin from the Maritime pine of France. For the simplication of the discussion the following assumptions were made:

1. That the oleoresin is composed only of essence (turpentine) and colophony (rosin);

2. That these components are both simple substances completely soluble in each other;

3. That neither is soluble in water; and

1. It is composed only of turpentine, pine oil,[2] and rosin;

2. The components are all simple substances completely soluble in one another;

3. None of the components are soluble in water;

4. The turpentine and pine oil are both volatile, but the turpentine has the lower boiling point;

5. Rosin is nonvolatile.

While these assumptions are not strictly true in all cases, none of them are sufficiently incorrect to affect seriously the conclusions.

Concerning the distillation with steam of the resinous material defined by the above assumptions the following deductions can be made:

1. There will be a separation of the two volatile constituents, the turpentine being in greater proportion in the first part of the distillate and the pine oil in the latter part;

2. The temperature of the distillation under normal pressure will be slightly above 95° C. at the beginning, and will rise throughout the distillation, never quite reaching 100° C., however, as long as any of the turpentine or pine oil remains undistilled;

3. If the pressure at which the distillation is carried on is increased the temperature will be increased, the temperature depending upon the pressure and on the concentrations of the turpentine, pine oil, and rosin; the temperature will, however, never reach the steam temperature corresponding to the pressures used as long as any turpentine or pine oil remains undistilled.

4. The proportion of water to oil in the distillate will increase as the distillation progressed, this proportion being influenced

4. That ro in is nonvolatile.

In regard to the oleoresin obtained by chipping the live longleaf pine tree of the United States, the same assumption can be made, but the oleoresin contained in the pitchy "lightwood" from this species has another component, the heavy, high-boiling "pine oil" which must be taken into consideration in the discussion of the steam distillation of such wood.

[2]A discussion of the occurrence of pine oil in the "lightwood" of longleaf pine is given in Forest Service Bulletin 105 ("Wood Turpentines, their Analysis, Refining and Composition," by L. F. Hawley).

only by the relative amounts of the different constituents present in the oleoresin being distilled.[1]

In these deductions it is considered that the system is in complete equilibrium and under such conditions the behavior of this oleoresin when distilled with steam could be foretold with considerable accuracy, but in the distillation of wood containing the oleoresin there is a disturbing factor introduced which makes necessary the investigation of the variables mentioned in the introduction. This disturbing factor is the difficulty of keeping a complete equilibrium between the oleoresin and the steam, due to the fact that the wood surrounds the oleoresin and tends to keep the steam from coming in contact with it.

The effects of the size of chips and the rapidity of distillation are not due to a change of the laws governing the distillation of the oleoresin with steam, but to the manner in which they affect the completeness of the equilibrium in the system, or in other words, the completeness of contact between the oleoresin and the steam. In the same way the effects (other than temperature changes) of steam pressure on the results of the distillation are also due to its influence on the completeness of contact between steam and oleoresin rather than to any influence on the behavior of the steam and oleoresin when completely in equilibrum.

EXPERIMENTAL METHODS. APPARATUS AND MATERIALS

The vertical cylindrical retort used for the distil'ations was three feet long by fifteen inches in diameter, with removable heads, the bottom head carrying a steam jet and the top head an outlet valve. A pressure gauge was inserted in the body of the retort. An ordinary worm condenser was used and the distillate was caught in one-liter graduated cylinders.

The general plan of the work was to distill charges of the same sized chips under different conditions or of different sized chips under the same conditions, noticing carefully the differences in the results of the distillations. It was not practicable to make

[1] A change in the pressure at which the distillation is carried on might change the proportion of water to oil in the distillate but this change would be only slight and there is not sufficient data available to decide even the direction of this change.

all the runs on comparable material on account of the difficulty in preparing a large number of charges of the same resin content and also on account of the difficulty of keeping the prepared material without loss of volatile oil by evaporation. The runs were therefore made in groups, all of the material used in each group being comparable. All the charges were prepared from a single log of pitchy longleaf pine in which the pitch was distributed with unusual regularity.

<div align="center">DISTILLATION</div>

Only a general description of the procedure will be given here; the same general methods were used in all cases and the details are given later in the tabulated record of the runs.

Data Obtained

A typical data sheet giving an example of the records obtained in each distillation is shown in Table 1. The distillate was caught in one-liter fractions and the time and pressure were recorded with every fraction. The amount of oil in each liter of distillate was determined as accurately as possible while in the original receiver (one-liter cylinders graduated to 10 cc.); the oil was then separated from the water in a separatory funnel and its specific gravity determined. When the amount of oil in the fractions was so small that a specific gravity determination could not readily be made on a single fraction the oil from a sufficient number of fractions was combined to make the determination possible. As a check on the total amount of oil computed from the rough measurements on the separate fractions the combined oil from all the fractions or from the fractions of different portions of the distillation was accurately measured.

The detailed records for each distillation will not be given in this report, but instead the essential part of this data will be tabulated together with other factors computed from the data. The discussion of the data from all groups will be taken up together after the experimental work has been described.

TABLE 1.—TYPICAL DATA SHEET, ILLUSTRATING THE
RECORDS TAKEN OF THE DISTILLATIONS

PROJECT 123—RUN No. 23
CHIPS 1″ x 2″ x 2″

Weight of can+water—   160 lbs.
Weight of can+water+chips—   215 lbs.   Steam turned on—   9.23
Weight of chips—   55 lbs.   Distillate began to flow—9.28.30

Time		Liters of Distillate	cc. of Oil in Distillate	cc. of Oil Total Computed	cc. of Oil Total Determined	Specific Gravity of Oil	Pressure
Hrs.	Min.						
9	36	1	88	88		.8810	70
9	48	2	154	242		.8794	72
9	59½	3	110	352	362	.8851	71
10	8	4	73	425			71
10	17	5	60	485		.8944	68
10	29½	6	55	540			71
10	40½	7	50	590		.8980	70
10	51½	8	44	634			72
11	½	9	39	673		.8981	70
11	8½	10	24	697			69
11	18½	11	27	724		.9010	72
11	28	12	26	750			69
11	38	13	19	769			72
11	47½	14	22	791			68
11	57½	15	17	808		.9016	69
12	7	16	17	825	839		69
12	17	17	16	841			69
12	27½	18	16	857			72
12	38½	19	18	875		.8987	72
12	50	20	19	894			64
1	0	21	15	909			71
1	9	22	13	922		.8965	72
1	18½	23	11	933			71
1	27½	24	10	943			69
1	39	25	12	955	979		68
1	48	26	10	965			70
2	0	27	11	976			70
2	11½	28	10	986			68
2	23½	29	12	998		.8958	72
2	34½	30	8	1006			73
2	45½	31	8	1016	1047		72
2	56½	32	10	1026			63
3	7½	33	13	1039			45
3	17	34	6	1045			32
3	26½	35	5	1050			20
3	37	36	4	1054		.8936	12
3	43	37	1	1055			4
3	45	38	1	1056	1095		0

TABLE 1.—*Continued.*

Time		Liters of Distillate	cc of Oil in Distillate	cc. of Oil Total Computed	cc of Oil Total Determined	Specific Gravity of Oil	Pressure
Hrs	Min						
Distilla	tion inte	rrupted	over night				
9	23½	39	22	1078		} .8934	72
9	35	40	17	1095			73
9	46	41	15	1110			71
9	57	42	10	1120			72
10	8	43	9	1129		} .9003	70
10	19	44	8	1137			72
10	30	45	7	1143		}	58
10	43	46	15	1158			34
10	53	47	8	1166		} .8935	19
11	4	48	6	1172			6
11	6	49	2	1174	1235	}	0

No of Liters	Yield cc lb	Efficiency
16	15.3	.95
25	17.8	.71
38	19.9	.51
49	22.4	.46

End Point

It will be noticed in Table 1 that the amount of oil in one liter of distillate gradually decreased and decreased very slowly toward the end of a distillation. On this account it became necessary to arbitrarily choose a ratio of oil to water which might be considered as the end of a distillation under one set of conditions in order to make the results of different distillations comparable and at the same time to keep the time required within practicable limits. In the first five runs the end point was too high and too variable, since it was not recognized that the end point must be very carefully regulated in order to obtain comparable results. These first five runs are, therefore, not comparable with those which follow in which the end point was carefully regulated at somewhat lower values. It was also found that after distilling a charge under one set of conditions until a certain end point was reached, if the distillation was interrupted for an hour or more and

TABLE II.—SUMMARY RECORD OF EXPERIMENTAL RUNS

Group No	Run No	Size of Chips	0 Lbs Pressure Yield cc per lb	0 Lbs Pressure Efficiency	20 and 30 Lbs Pressure Yield cc per lb	20 and 30 Lbs Pressure Efficiency	40 and 50 Lbs Pressure Yield cc per lb	40 and 50 Lbs Pressure Efficiency	70 Lbs Pressure Yield cc per lb	70 Lbs Pressure Efficiency	Total Yield cc per lb	Total Efficiency	Speed Min per Liter	End Point cc per Liter
I	1	Sawdust	20.6	1.71			9.9c	.45			30.5	.90	4	25 and 12
	2	Sawdust					32.7c	1.26			32.7	1.26	4	18
	3	Sawdust	12.5	1.56			8.2c	.41			20.7	.74	4	17 and 12
	4	2"x1"x1"	6.4	.61	5.8a	.45	3.9c	.33	20.3	.33	20.3	.33	5	12
	5	2"x¼"x⅛"	8.0	.55	5.1a	.28	6.1c	.24	9.1	.33	25.2	.38	4	12
	6	2"x¼"x⅛"	15.7	.63	4.6a	.29	5.3c	.24			19.2	.34	10	10
	7	1"x¼"x⅛"	10.2	.46	6.5a	.25	6.2c	.19			25.6	.40	10	10
	8	1"x¼"x⅛"			22.4b	.46	3.0d	.19	4.5	.21	23.0	.29	10	10
	9	1"x¼"x⅛"					27.2d	.46	1.5	.12	29.9	.34	10	10
	10	1"x¼"x¼"									28.7	.40	10	10
II	11	Sawdust	27.7	1.46			2.0c	.25			29.7	1.1	10	10
	12	1"x variable							25.7	.49	25.7	.49	10	10
	13	6"x variable							12.3	.29	12.3	.29	10	10
III	14	1"x5"x8"					19.7d	.35	5.9	.17	25.6	.28	10	10
	15	1"x½"x1½"					24.5d	.41	4.7	.15	29.2	.32	10	10
IV	16	Sawdust	25.2	.97	24.5b	.50	4.0c	.31			29.1	.75	10	10
	17	1"x¼"x⅛"					26.8d	.50					10	10
	18	1"x¼"x⅛"					25.3d	.55					10	10
	19	1"x¼"x¼"											10	10
	20	1"x¼"x¼"							29.8	.63	29.8	.63	10	10
V	21	Sawdust	24.6	1.05			1.7c	.23			26.3	.82	10	10
	22	1"x2"x2"							23.1	.39	23.1	.39	10	10
	23	1"x2"x2"							22.4	.46	22.4	.46	10	10

a=20 lbs.   b=30 lbs.   c=40 lbs.   d=50 lbs.

Table II.—Summary Record of Experimental Runs—*Continued*

Group No.	Run No.	Size of Chips	0 Lbs Pressure Yield oo per lb	0 Lbs Pressure Efficiency	20 and 30 Lbs Pressure Yield oo per lb	20 and 30 Lbs Pressure Efficiency	40 and 50 Lbs Pressure Yield oo per lb	40 and 50 Lbs Pressure Efficiency	70 Lbs Pressure Yield oo per lb	70 Lbs Pressure Efficiency	Total Yield oo per lb	Total Efficiency	Speed Min per Liter	End Point cc per Liter
VI	24	1″ x 4″ x 4″	....	....	....	....	....	....	23 6	.44	23.8	.44	10	10
	25	Sawdust	24.0	.89	....	....	2.6°	.26	....	....	26.6	.70	10	10
	26	1″ x 1″ x 1″	....	....	....	....	....	....	22.8	.45	22.8	.45	10	10
	27	2″ x 1″ x 1″	....	....	....	....	....	....	21.4	.31	21.4	.31	10	10
	28	3″ x 1″ x 1″	....	....	....	....	....	....	12.9	.29	12.9	.29	10	10
	29	Sawdust	19.3	.84	....	....	1.7°	.17	....	....	21.0	.64	10	10
	30	Shavings	18.8	.94	....	....	....	....	....	....	....	....	6	5
			.6										10	7
			19.4	.85									6 and 10	5 and 7
VII	31	Shavings	16.0	.84	....	....	3.1°	.39	....	....	22.5	.73	3	5
			1.4										10	7
			17.4	.70									3 and 10	5 and 7
	32	1″ x ½″ x ½″	....	....	....	....	....	....	20.1				6	5
									.7				10	7
									20.8	.43	21.2	.60	6 and 10	5 and 7
	33	1″ x ½″ x ½″	....	....	....	....	3.8°	.38	18.1	.39	20.8	.39	3	5
									2.2	.39			10	7
									20.3	.33	20.3	.33	3 and 10	5 and 7

a = 20 lbs.   b = 30 lbs.   c = 40 lbs.   d = 50 lbs.

then continued under the same conditions as before, a further supply of oil could be obtained before the same end point was reached again. This additional amount of oil obtained as a result of interrupting the distillation amounted to from 2 per cent to 18.8 per cent of the oil already obtained before the distillation was interrupted. The highest increases in yields due to this manipulation were those runs where there was still considerable oil present in the wood when the distillation was interrupted (although, of course, all the oil possible had been removed under the prevailing conditions). For instance, in Runs 14 and 15, after all the oil possible had been distilled at 50-pounds pressure, interruption of the distillations over night made it possible to distill respectively 18.8 per cent and 15.1 per cent more oil under the same conditions; in both these cases there was still considerable oil present in the wood as shown by further distillation at increased pressures. In Runs 11 and 21, however, after all the oil possible had been distilled at atmospheric pressure, interruption of the distillations made it possible to obtain only 2.9 per cent and 4.0 per cent more oil under the same conditions; in these cases there were much smaller quantities of oil left in the wood than in Runs 14 and 15.

This effect also was not recognized as important until after Run 5 was finished, so that for another reason Runs 1 to 5 are not comparable with those which follow.

The proper end point for any distillation after Run 5 was considered to be reached only when the required ratio of oil to water in the distillate had been attained both before and after interruption of the distillation.

DISCUSSION OF RESULTS

The data obtained by the distillation of the various runs are g'ven in Table 2 together with the conditions under which the distillations were made. In the table the size of the chip as given in column two is expressed in inches with the length parallel to the grain given first. The values given in the columns headed "Yield" are expressed in cc. of oil per pound of wood. The possible error in these determinations of yields is apparently about 6 to 7 per cent and is due to difficulties in sampling, in regulating

evaporation during the preparation of material, and in obtaining comparable end points in different distillations.

An example of results which must be due to such errors is seen in Runs 23 and 24. The chips in Run 24 are larger than those in Run 23 and the yield should be perhaps less and certainly not greater from the larger chips, and yet the yields obtained from Run 23 are 5.0 per cent less than those from Run 24. Another similar example is shown in Runs 30 and 31. It might be thought that some of these variations in yields were due to incomplete distillation caused by the "channeling" of the steam through the charge in such a way that part of the wood was never touched by the steam, but in several runs after all the oil possible had been distilled under some one set of conditions the top of the retort was removed, the charge well stirred, and the distillation continued under the same conditions as before without any indications that the stirring had discovered undistilled material in the charge. It seems probable, therefore, that with a retort of the shape and size used in these distillations the effect of incomplete distillation due to incomplete contact between the steam and the surface of the chips is negligible.

TABLE 3.—EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY

Run No	Size of Chip	Pressures	Yields	Efficiency	Speed Min Per Liter	End Point cc Oil Per Liter Distillate
7 8	1″ x ¼″ x ⅛″ 1″ x ½″ x ¼″ }	atmospheric	{ 15.7 10.2	.63 .46 }	10	10
12 13	1″ sections from slabs 6″ sections from same }	70 pounds	{ 25.7 12.3	.49 .29 }	10	10
14 15	1″ x 5″ x 8″ 1″ x 1½″ x 1½″ }	50 pounds	{ 19.7 24.5	.35 .41 }	10	10
26 27 28	1″ x 1″ x 1″ 2″ x 1″ x 1″ 3″ x 1″ x 1″ }	70 pounds	{ 22.8 21.4 12.9	.45 .31 .29 }	10	10

The values given under "Efficiency" are obtained by dividing the yields per pound of wood by the number of liters of total distillate, the efficiency factor being cc. oil per pound of wood

TABLE 4.—EFFECT OF PRESSURE ON YIELD AND EFFICIENCY

Run No	Size of Chip	Pressures	Yields	Effic- iency	Speed Min Per Liter	End Point cc Oil Per Liter Distillate
8	$1'' \times \frac{1}{2}'' \times \frac{1}{4}''$	Atmospheric	10 2	.46	10	10
9	$1'' \times \frac{1}{2}'' \times \frac{1}{4}''$	30 pounds	22.4	.46	10	10
10	$1'' \times \frac{1}{2}'' \times \frac{1}{4}''$	50 pounds	27.2	.46	10	10
17	$1'' \times \frac{1}{4}'' \times \frac{1}{8}''$	30 pounds	24.5	.50	10	10
18	$1'' \times \frac{1}{4}'' \times \frac{1}{8}''$	50 pounds	26.8	.50	10	10
19	$1'' \times \frac{1}{2}'' \times \frac{1}{2}''$	50 pounds	25.3	.55	10	10
20	$1'' \times \frac{1}{2}'' \times \frac{1}{2}''$	70 pounds	29.8	.63	10	10

per liter of distilate or $\frac{cc\ oil}{pounds\ wood\ \times\ liters\ distillate}$. It might be thought that this "efficiency factor" would have more significance if it represented only the relation between oil and total distillate, but, as will be seen later,[1] this relation would be affected by the amount of wood distilled. Of course, the effect may not be in 'exact proportion to the amount of wood distilled as represented in the factor used, but it is thought that more nearly comparable efficiency factors are obtained by including the amount of wood as above. These factors represent approximately the relative amounts of oil obtained in the different runs per unit of steam consumed, exclusive of the steam which supplies the heat lost by radiation.

EFFECT OF SIZE OF CHIP ON YIELD AND EFFICIENCY

In general, other conditions being the same, the smaller the chip, the larger the yields and the higher the efficiency. This is shown in Table 3 which contains selected data from Table 2. Four groups of distillations are given, in each of which all the other conditions except size of chip are as nearly as possible the same, and in every case the smaller-sized chips show the larger yield and higher efficiency. The effect on yield is not so marked in the case of Runs 26 and 27 (and some of the other runs given in Table 2) but this is accounted for by the fact that the pressure was high enough so that nearly all the oil was removed even from

[1]The same reasoning as is given on page 168 regarding the effect of the size of retort on the efficiency applies also to the effect of the amount of wood distilled on the efficiency.

the larger-sized chips. In the case of two runs in which all the oil was removed even from the larger chips the yields would of course be the same, but the efficiency would probably be higher with the smaller-sized chips.

EFFECT OF PRESSURE ON YIELD AND EFFICIENCY

In general, other conditions being the same, higher pressures give larger yields without lowering the efficiency. This is shown in Table 4 which gives three groups of runs, in each of which all conditions except steam pressure are as nearly as possible the same. In all cases the higher steam pressure produced the larger yield and with the same or higher efficiency. The effect of pressure on yields is also shown in another way in many of the runs in Table 2 in which after obtaining all the oil possible by distilling under one pressure a further yield of oil was obtained by continuing the distillation under a higher pressure.

EFFECT OF SPEED OF DISTILLATION ON YIELDS AND EFFICIENCY

Other conditions being the same, increased speed of distillation decreases both the yield and the efficiency. This is shown clearly in Table 5 which gives the results of two sets of two runs each, all the conditions except the speed being the same in each set. The more rapid passage of the steam through the charge probably causes it to be less completely saturated with the oil vapors, thus directly decreasing the efficiency. The yield is decreased probably because the same end point is reached sooner when the steam is less completely saturated. This is indicated by the more nearly equal total yields obtained in each set of runs by finishing up the distillations at the same pressure but at lower speeds. The variation in efficiency is not, however, as might be expected, exactly proportional to the speed, since doubling the speed decreases the efficiency by only about 10 per cent, from .94 to .84 in Runs 30 and 31, and from .43 to .39 in Runs 32 and 33.

If, as seems probable, the effects of speed are due to the variations in the time during which the steam is in contact with the

wood. then the size of the retort would have a similar effect; that is, a speed of 10 minutes per liter in a certain sized retort would be equivalent to 5 minutes per liter in a retort twice as large, since a unit of steam would be in contact with a unit of wood for the same length of time in either case.

TABLE 5.—EFFECT OF SPEED ON YIELD AND EFFICIENCY

Run No	Size of Material	Pressure	Speed Min Per Liter	End point cc Oil per Liter	Yield	Total Yield	Efficiency	Total Efficiency
30	Shavings	Atmospheric	6	5	18 8	18.8	.94	.94
		Atmospheric	10	7	.6	19.4	...	.85
		40 pounds	10	10	3.1	22.5	.39	.73
31	Shavings	Atmospheric	3	5	16.0	16.0	.84	.84
		Atmospheric	10	7	1.4	17.4	...	.70
		40 pounds	10	10	3.8	21.2	.38	.60
32	1″ x ½″ x ½″	70 pounds	6	5	20.1	20.1	.43	.43
			10	7	.7	20.8	...	.39
33	1″ x ½″ x ½″	70 pounds	3	5	18.1	18.1	.39	.39
			10	7	2.2	20.3	...	.33

RELATIONS BETWEEN END POINT, YIELD AND EFFICIENCY

As shown in Table 1 the amount of oil in a liter of total distillate is greatest at the beginning of the distillation and decreases steadily as the distillation progresses. except when the conditions of distillation are changed, and then the increase in the amount of oil per liter is usually only slight and temporary. This was true in all the distillations and it is evident, therefore, that the efficiency factor will decrease steadily throughout the distillation and its final value will depend on the end point used. Therefore, the efficiency can be increased by stopping the distillation before all the oil possible has been obtained and thus decreasing the total yield of oil. For the same reason the efficiency will be decreased by continuing the distillation until all the oil possible has been obtained and thus increasing the total yield of oil. For instance, in Run No. 23 (Table 2) if the distillation had been stopped with an end point of 12 cc. per liter,

at the 25th liter the yield would have been only 15.3 cc. per pound
while the efficiency would have been .95. By continuing the
distillation until the end point (after an interruption of the dis-
tillation) was 10 cc. per liter, a much larger yield, 22.4 cc. per pound
was obtained, but only at the expense of much decreased effi-
ciency (.46).

<div align="center">THE PRESSURES REQUIRED TO DISTILL COMPLETELY
DIFFERENT SIZES OF MATERIAL</div>

Sawdust

The volatile oil cannot be completely distilled at atmospheric
pressure even from a material as finely divided as sawdust. This
can be seen from Runs 11, 16, 21, 25, and 29, in which, after re-
moving all the oil possible at atmospheric pressure, a further
distillation at 40 pounds pressure removed from 6.6 to 15.8 per
cent more oil. It was found that after distilling at 40 pounds
pressure a further distillation at 70 pounds was without appre-
ciable effect. It can be safely stated that 40 pounds pressure is
sufficient for the removal of all the volatile oil from material as
small as sawdust. It is possible that lower pressures might give
almost as good results but this point can not be determined from
the data on hand.

Chips $1''x\frac{1}{4}''x\frac{1}{8}''$

This size material cannot be completely distilled at 30 pounds
pounds pressure (Run 17) and probably not at 50 pounds pressure
(Run 18). In Run 18 the yield obtained from chips $1''x\frac{1}{4}''x\frac{1}{8}''$
is almost the same, within the limit of possible variation, as from
the sawdust of Run 16, but apparently not quite all the oil has
been removed.

Chips $1''x\frac{1}{2}''x\frac{1}{2}''$

Chips of this size cannot be completaly distilled at 50 pounds
pressure (Run 19) but can at 70 pounds (Runs 20, 32, and 33).

Chips larger than $1''x\frac{1}{2}''x\frac{1}{2}''$

At the maximum pressure used, 70 pounds, chips larger than
$1''x\frac{1}{2}''x\frac{1}{2}''$ cannot be completely distilled, but as the size of chips
is increased there is no sudden drop in the yields obtainable at
this pressure until sizes larger than 2 inches with the grain (Runs

27 and 28)[1] and 4 by 4 inches across the grain are used (Runs
14 and 24). It is probable that 80 to 85 per cent of the oil could
be removed from chips 2″x4″x4″ by distillation at 70 pounds
pressure.

EFFECT OF PRESSURE ON COMPOSITION OF OIL

Analyses were made by the method described in Bulletin 105
of part or all of the oil from each of the runs, but there was not
enough difference between the various samples so that all of the
analyses will need to be given. A few distillation curves showing
the main points of interest will be given.

Pine Oil

The proportion of pine oil in the crude turpentine did not vary
except in cases which could be explained by variation in other
factors besides pressure and, therefore, so far as the results show,
the pressure has no influence on the proportion of pine oil except
the influence due to increasing the total yields. In all cases where
the total oil obtained was analyzed, and where the oil was nearly
completely removed from the wood, the percentage of pine oil
by weight varied only between 48 per cent and 52 per cent.[2]
In cases where only part of the oil was removed by the distillation,
as in Run 4, the proportion of pine oil was less.

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[1]In determining the percentage of total oil obtained in the runs of Group
VI it must be remembered that the sawdust of Run 25 was not exactly a
representative sample of the material of that group but that it was mixed
with the sawdust obtained in cutting the slabs from the blocks. In several
cases similar samples of sawdust obtained in cutting the slabs had been dis-
tilled and found to contain more volatile oil than the sawdust obtained in
cutting the blocks. It is probable, therefore, that the proportion of volatile
oil in the mixed sample of sawdust was somewhat greater than in the rest of
the material in this group. This point is further indicated by a comparison of
the yields obtained from the sawdust runs in the different groups. With the
exception of Group VI (Run 25) the yields from the sawdust decrease, as might
be expected for the reason that the material for the groups was cut from the
same log in order of the group number, beginning at the butt end and the con-
tent of volatile oil in the butt end was higher than in the upper portions of
the log. It is probable, therefore, that a value of 24 to 25 cc. oil per pound
of wood would more nearly represent the volatile oil content of the group.
[2]Exceptions were found to this in the oils from Group II which contained
about 28 per cent pine oil. But the material for this group did not repre-
sent a complete cross section of the log, being composed instead only of the
outside pieces, the slabs. The outer layers of this log evidently contained
a smaller proportion of pine oil than the rest of the wood.
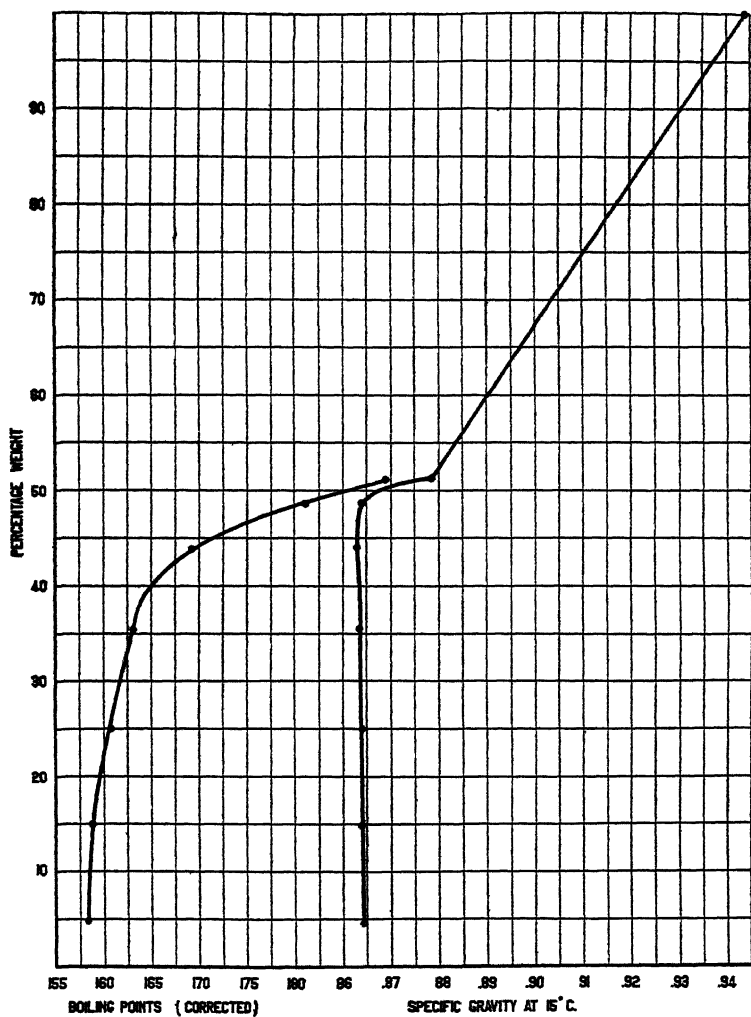
Figure 1. BOILING POINT AND SPECIFIC GRAVITY CURVES FOR OIL FROM RUN 21

Dipentene

The detection of small differences in the proportion of dipentene present cannot be made by the method of examination used, especially when such large proportions of pine oil are present. There seemed to be, however, more dipentene in the crude turpentines produced at higher pressures. Figures 1 and 2, representing the distillation curves obtained in the analyses of the oils from Runs 21 and 23, respectively, illustrate this point. The oil obtained from sawdust mostly at atmospheric pressure (Figure 2) apparently contains less dipentene than the oil distilled entirely at 70 pounds pressure (Figure 2); the specific gravity values being lower and the proportion of the oil boiling between 165° and 180° larger in the latter case. It had formerly been thought that the dipentene which had been found in wood turpentines was caused by the temperature used in distilling the oil from the wood, but indications of dipentene were found in all the samples of oil obtained in this investigation, even in those produced at atmospheric pressure, and it is very probable that dipentene was present as such in the wood distilled. In order to make sure that this material with low specific gravity and high-boiling point was dipentene and not some other terpene with similar physical properties, a chemical examination was made of the fractions 165° to 185° from some of the turpentines produced at atmospheric pressure and dipentene was identified by means of the tetrabromide, M. P., 125°-126°.

In order to determine the possibility of the transformation of pinene into dipentene under the condition of steam distillation the sawdust from Run 29 was air dried and moistened with 1175 cc. of gum turpentine (an amount equal to the total volatile oil originally present) and distilled at atmospheric pressure. The oil on analysis showed no indications of dipentene. The experiment was repeated, making the distillation at 50 pounds pressure, but with the same result. These results preclude the possibility of formation of dipentene from pinene under the conditions of steam distillation pressures below 50 pounds and indicate very strongly that dipentene occurs as such in lightwood.

Light Oils

Figures 1 and 2 also illustrate another effect of pressure on
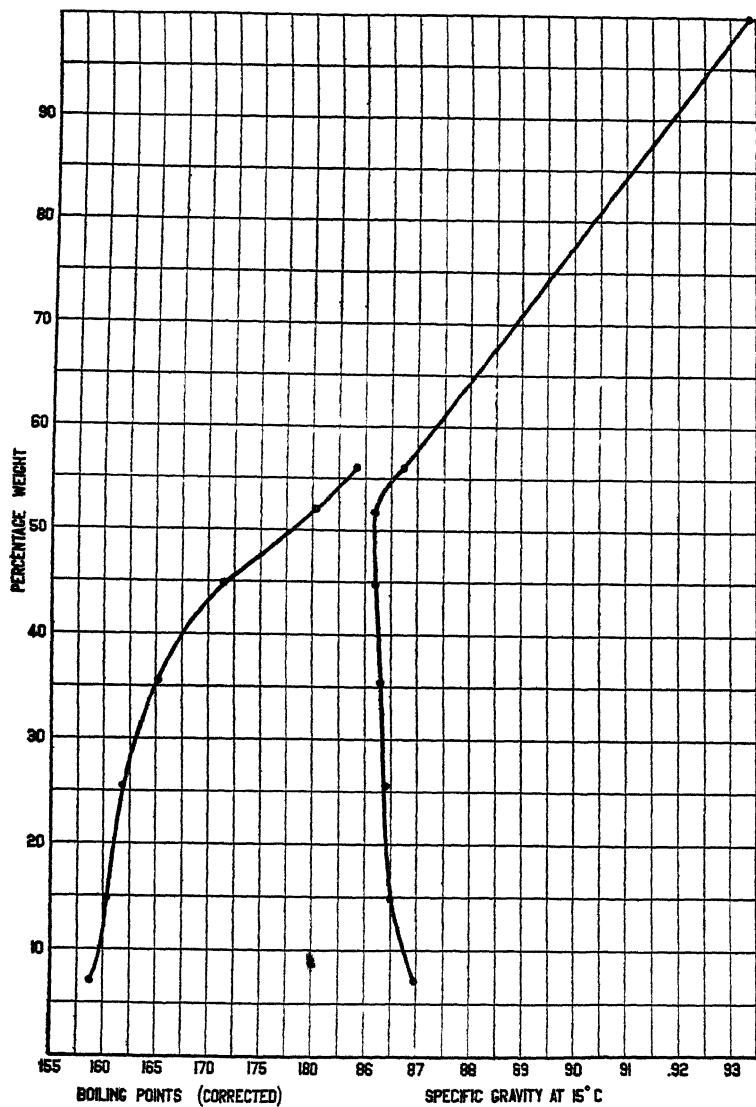
Figure 2. BOILING POINT AND SPECIFIC GRAVITY CURVES FOR OIL FROM
RUN 21

the composition of the crude turpentines. In these analyses, as in many others, the crude turpentines produced at pressures as high as 70 pounds show a considerably higher value for the specific gravity of the first fraction than do the turpentines produced at lower pressures. This indicates that some substance with low-boiling point and high gravity (above .870 at 15° C.) is produced at the higher pressures; this substance might come from the incipient decomposition of some portion of the resin at the temperature to which it is subjected. The first fractions from the analyses which contained this substance were slightly yellow and had a peculiar odor, different from the rest of the fractions. A treatment with caustic soda reduced the gravity of these fractions but increased the yellow color. It was found, however, that by the treatment of a turpentine like that shown in Figure 2 with caustic soda followed by a distillation it was possible to prepare a refined turpentine which showed no abnormality of the first fraction in color, odor, or gravity. The presence of this substance should not, therefore, introduce any difficulty in the refining process.

Another test for the presence of decomposition products was made on several of the samples produced at different pressures by treating the oil with concentrated hydrochloric acid; a red color produced in this way is supposed to indicate the presence of rosin oil. There was only a very slight coloration of the oils produced at atmospheric pressure, but this coloration increased with the pressure, becoming very marked in the oils produced at 50 pounds and 70 pounds pressure.

FRACTIONATION OF THE OIL DURING DISTILLATION

Some very interesting conclusions regarding the details of the manner in which the volatile oil leaves the wood can be obtained by comparing the values of the specific gravity of various portions of the distillate. As was previously stated the specific gravity of the oil was determined from each liter of distillate, or from as many liters as were necessary to furnish the amount of oil required for a determination. Figures 3, 4 and 5 show these values of the specific gravity obtained in Runs 16, 20 and 7, respectively, plotted against the percentages of the total oil obtained.
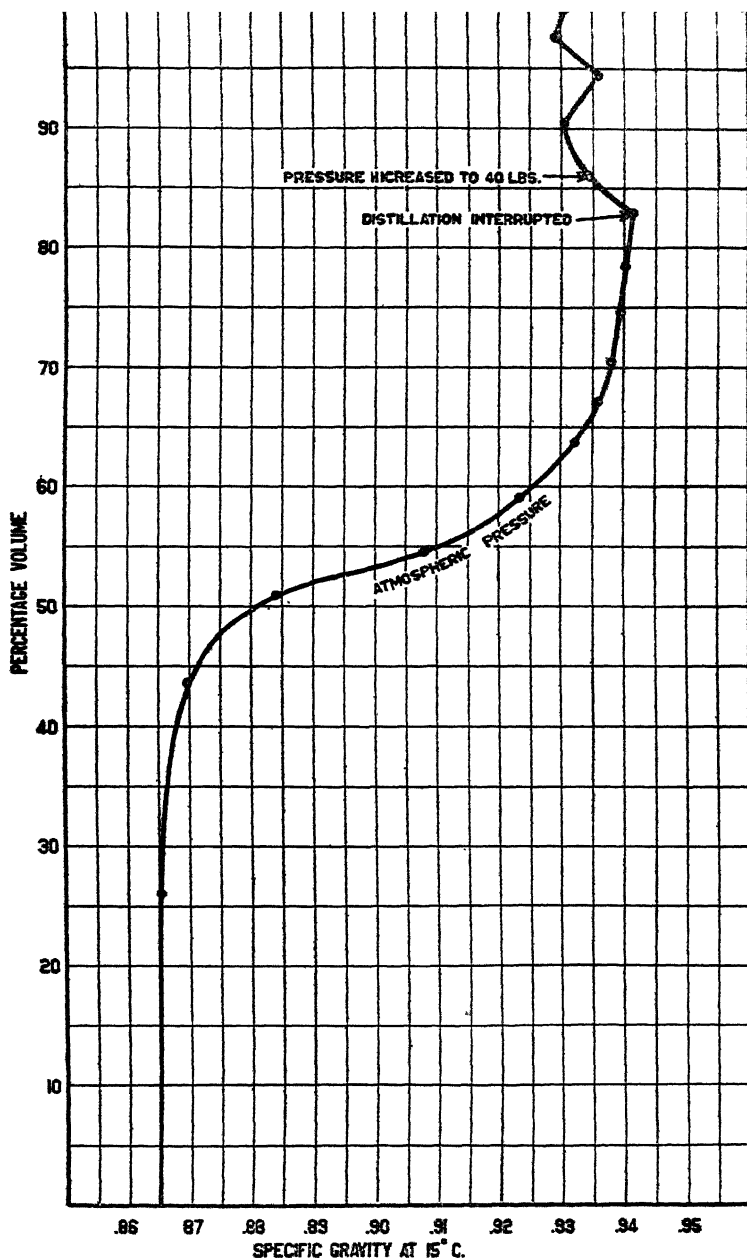
Figure 3. Curve Showing Fractionation of Oil During Run 16

Figure 3 shows the changes in the specific gravity of the oil obtained during the distillation of a charge of sawdust, first at atmospheric pressure, and then at 40 pounds pressure. The first portions of the oil were nearly pure turpentine, but after about 44 per cent had been distilled the gravity increased rapidly, indicating the presence of pine oil in increasing quantities; when the distillation was from about 67 per cent to 83 per cent completed the oil was nearly pure pine oil. The part of the curve up to 83 per cent resembles very closely the distillation curve which could be obtained from the distillation with steam of a crude turpentine; that is, the presence of the wood seems to have no effect on the manner in which the volatile oils are distilled. A difference is seen, however, in that portion of the curve beyond 83 per cent; after practically all the oil possible had been removed by a continuous distillation at atmospheric pressure, the interruption of the distillation followed by a further distillation under the same pressure produced a small further yield of oil with a lower gravity, and on increasing the steam pressure still more oil was obtained with a still lower gravity. This indicates that both the interruption of the distillation and the increase in steam pressure brought more oil into contact with the steam and that this oil contained some of the low-gravity turpentine material.

A very different behavior is shown in Figure 4, which represents the distillation of chips $1''x\frac{1}{2}''x\frac{1}{2}''$ at a pressure of 70 pounds. In distillation under these conditions there was much less tendency for the oil to be separated as it is distilled, the gravity of the very first fraction being higher than that of pure turpentine and the gravity of the later fractions never reaching that of pure oil; that is, the turpentine and pine oil distilled together throughout the run. This indicates that new supplies of volatile oils were brought into contact with the steam more or less continuously throughout the distillation, since otherwise the turpentine would have distilled first and the last fractions would have been nearly pure pine oil.

A still more striking picture of the variation in the gravity of the distillate due to changes in the conditions of distillation is shown in Figure 5; this represents the gravities of different parts of the oil obtained during the distillation of chips $1''x\frac{1}{4}''x\frac{1}{8}''$ at
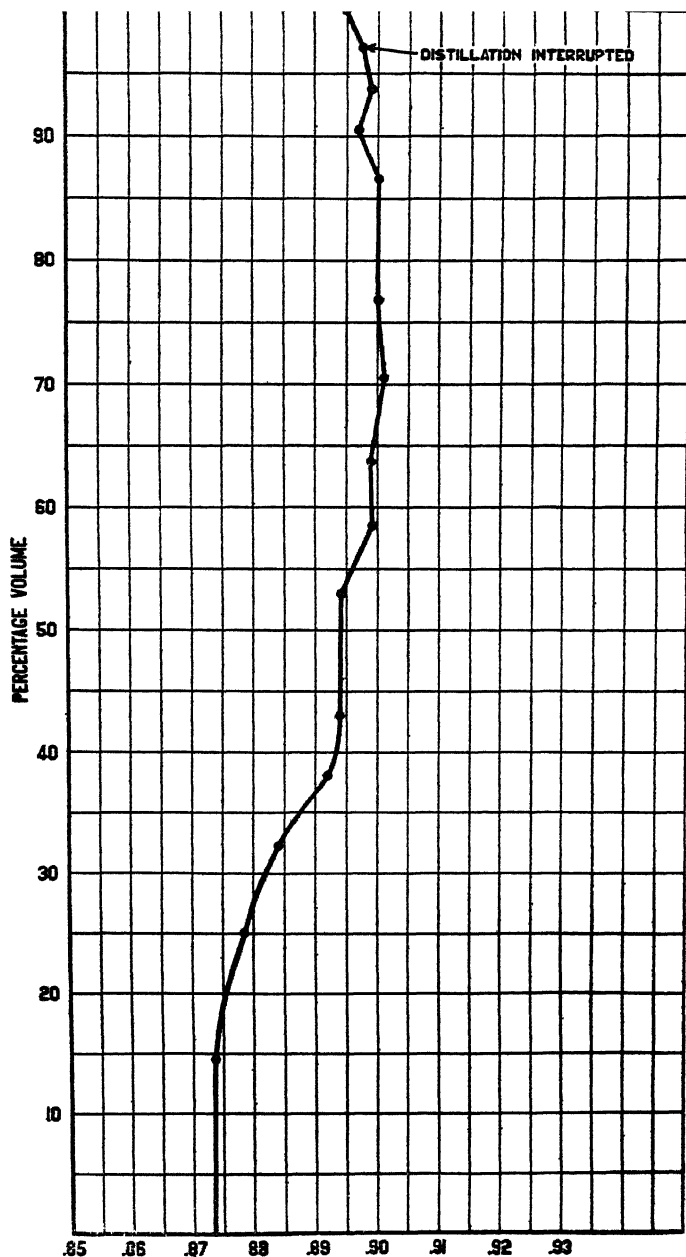
Figure 4. CURVE SHOWING FRACTIONATION OF OIL DURING RUN 20

atmospheric, at 20 pounds, and then at 40 pounds pressure. During the first of the run at atmospheric pressure the gravity gradually increased, but never quite reached that of pure pine oil. By a continuous distillation at atmospheric pressure only about 50.5 per cent of the total oil could be removed, but on interrupting the distillation for about fourteen hours and continuing again at atmospheric pressure 7 per cent more oil was obtained, the gravity of the first part of this 7 per cent being much lower and of the last part only slightly lower than that of the last fraction of the continuous run. On increasing the pressure to 20 pounds, about 16.8 per cent more oil was obtained, the gravity suddenly dropping and then gradually rising during the distillation of this 16.8 per cent. On increasing the pressure to 40 pounds and distilling continuously, a further yield of 19.5 per cent was obtained, the gravity of this 19.5 per cent dropping suddenly at first and then gradually rising. A similar additional yield was obtained by another interruption of the distillation, about 6 per cent more oil being obtained.

Here again the effect of interrupting the distillation and of increasing the pressure are very plainly shown, viz., increased yield of oil with gravity lower than the last fraction obtained before the conditions were changed.

This effect of the increased pressure in increasing the yields is due then to bringing more steam and oil into contact with each other than is possible at lower pressures. This could result either from a penetration of the steam further into the wood at the higher pressures or from a flow of resin toward the surface of the wood due to the decreased viscosity at the higher temperatures. It seems probable that both these have some influence, but the effect of the latter is quite certain, since it was noticeable that in the distillations made at high pressures a considerable amount of rosin would collect in the bottom of the retort or the outside of many of the chips would be coated with thin layers of rosin.

The effect due to the interruption of the distillation and continuing it again under the same conditions can not be explained so readily, but it is probably due to a slow flow of rosin toward the surface or to the diffusion of the volatile oils in the rosin from
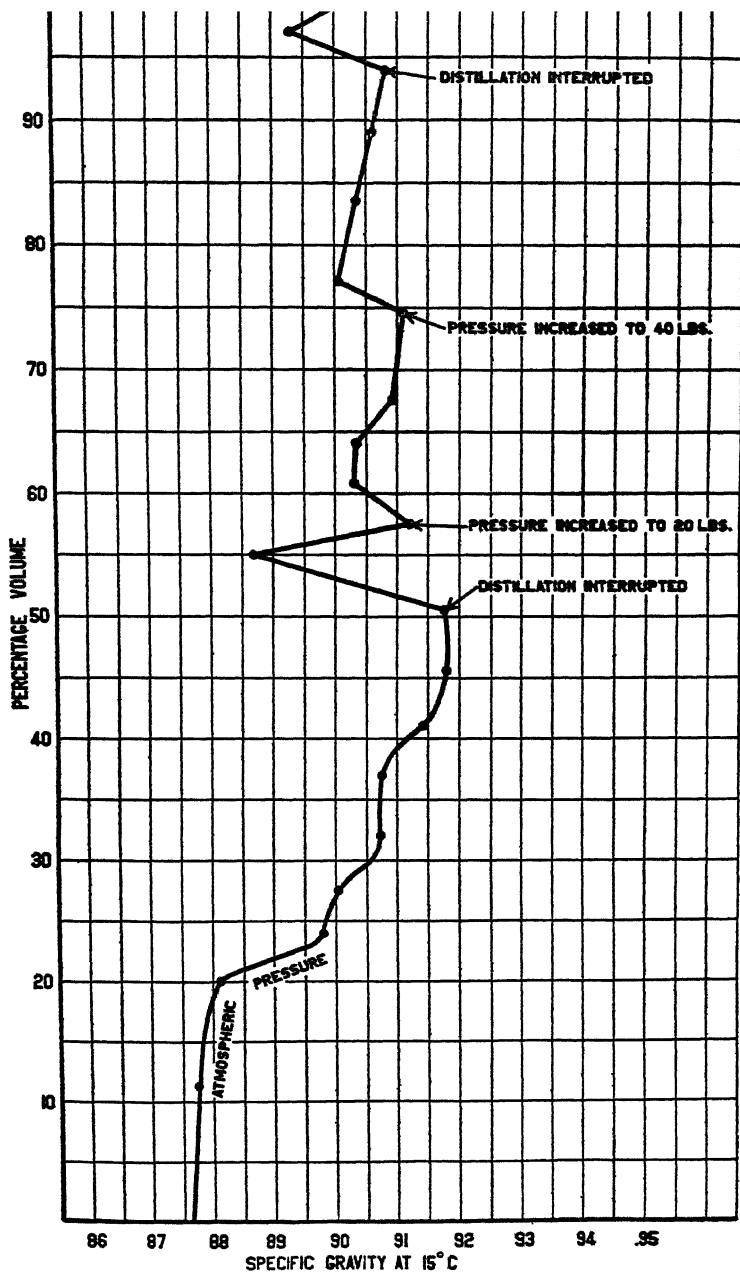
Figure 5. CURVE SHOWING FRACTIONATION OF OIL DURING RUN 7

the interior of the chip to the rosin at the surface from which the oil has been removed.

APPLICATION OF RESULTS

The foregoing discussions have considered the effects of the different variables (1) size of chip, (2) pressure of steam, (3) speed of distillation, and (4) end point at which distillation is stopped, on (a) the yield of total oil, (b) the composition of the oil, and (c) the amount of steam required to remove the oil. It can be seen that there should be a certain combination of values for these variables which would give a most economical method of operation for a steam distillation plant; but there are other factors which must be taken into consideration in determining the proper combination of values. For instance, the best size of the chip will not be determined entirely by the effect of size on yield and efficiency, but also by the relative costs of preparing different sized chips and the use to which the chips are to be put after steaming; the best pressure of steam will not be determined entirely by the effect of pressure on yield and efficiency, but also by the relative costs of high and low pressure steam and of apparatus designed for use with different pressures; the best speed for the distillation will not depend entirely upon the effect of speed on the yield of products and on the amount of steam required, but also upon the cost of steam and the overhead charges; the best end point at which to stop the distillation will not depend entirely upon the effect of end point on yield and efficiency, but also upon the cost of the raw material, the value of the products, etc.

Sufficient experimental data have been given, however, so that a knowledge of the various cost factors mentioned above (which would naturally vary a great deal in different plants) would make it possible to decide readily on the most economical methods for operating.

MODIFIED STARCH

By B. Herstein

Tariff Board, Washington, D. C.

The colloidal nature of starch was recognized very early and, like many other colloids, starch is capable of existing in several modified forms. The differences in form here referred to are not those known to be of botanical origin and due to the different plants the starch is derived from. Such differences, although characteristic for each starch, are due only to the size, the number of molecules forming a given granule of starch and their distribution in space. The variations in structure and in optical behavior of starches from different sources are sufficiently explained under some such assumption. Moreover, these variations existing already in a performed condition, are not and cannot be brought about by artificial agencies.

Changes in form on the other hand, spoken of nowadays as colloidal, are of a more far-reaching character; they affect the equilibrium of the aggregation of molecules, and are caused by foreign reagents.

But even with this limitation it is difficult to convey a concrete conception of the term "Modified Starch" as used here, and this is largely due to the peculiar nature of starch as a chemical entity. After a century of intrusive investigation, our knowledge of this most important plant secretion is still very limited indeed in this direction, owing again to the fact that the changes in form which the starch undergoes under the influence of reagents are very gradual, indistinct and almost intangible.

The most specific properties of starch are:

(*a*) Physical; ability to gelatinize with water or to form viscous solutions therewith, and to show color reactions with iodine.[1]

(*b*) Chemical; ability to become hydrolyzed with diastase to maltose and with acids to dextrose.

[1] It must not necessarily be a blue color, because there are natural starches, like panicum miliaceum glutinosum and cryzem glutinosum which give a red brown color with iodine solutions.

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Any product derived from starch showing essentially all or most of these characteristics would come under the heading of "Modified Starch" irrespective of the process used in its preparation, and if this viewpoint is correct the whole group of derivatives, isolated or supposed to have been isolated from starch and constituting gradual disintegration products from starch until the maltose stage is reached, will fall under this classification.

In this sense we would apply the term "Modified Starch" to the "granulose" of mægeli, the "amylose" of Meyer, the "amiduline" of Nasse, the many forms of soluble starch prepared with the aid of either acids or alkalies or of boiling glycerol, the so-called "Thin Boiling" starches, the great number of dextrins including the maltodextrin and amylodextrin, whether they be obtained by torrefaction or by inversion with either acid or an infusion of malt, and, lastly, also the many products isolated under different names by the laborious method of repeated precipitation with alcohol by a host of indefatigable investigators, who tried to shed light on that extremely complex chemical problem comprised within the syllable starch.

There will be little if any objection to this classification as far as the soluble starches are concerned, though some opposition might be expressed with reference to the dextrins. Yet these latter, upon sufficient reflection, will not show more divergence from starch, either qualitatively or quantitatively, than the former. The difference is physical only in either case. While soluble starch differs materially in the fluidity of its aqueous solution from that of starch, the dextrins deviate only in their color reaction with iodine as against that of starch or rather that of standard starch. As shown in preceding foot note, there are starches showing very brown colorations with iodine, or exactly the same as obtained with most of the dextrins. The only other difference between these substances is that the dextrins, as a rule, form apparently perfectly homogenous and transparent solutions with water, while the solutions of soluble and of normal starch are more or less translucent. Chemically, however, they all show the same composition and behavior, especially since it was shown that the dextrins like the rest are hydrolyzed by malt infusions. The principal support, however, for the view expressed by many inves-

tigators and maintained here, namely, that all the products mentioned are but modified forms of starch, *i.e.*, where the original molecule has remained intact, is found in the fact that all the products enumerated show the same rotation of polarized light, equal to that of normal starch. As the degree of disintegration of the starch molecule is, as a rule, in inverse proportion to the rotary power of the products obtained, the substances before mentioned cannot have undergone any considerable breaking up. In view of this, no further justification would seem to be necessary when the term "Modified Starch" is applied here as a generic classification.

In the group of products treated hitherto and comprised within the limits of starch on one side, and maltose on the other, a gradual even if very slow tendency toward degradation and disintegration of the original starch is unmistakable. The processes used in their preparation furthermore make such a disintegration highly probable.

But there exists another group of substances obtained from starch by methods so slow in their effect that any deep going disruption would seem to be precluded. They are substances differing in some physical characteristics from normal starch, though otherwise they are still starch with the same chemical properties, the same optical rotation, where observable, as starch, and showing the same color reaction with iodine as starch. They too are modified starches only. The peculiar feature of these products is their inability to form viscous aqueous solutions or pastes, and in one particular form—to be treated more in detail later—absolute insolubility in either water or alkalies. First to be noted in this group are the products obtained by the action of slightly superheated steam on starch, followed by drying. The starch is in this process rendered almost insoluble in water and is also deprived of the property of forming a paste. Another form of modified starch belonging here and one which might properly be called the anticlimax, to the one preceding, is the product obtained from a fairly thick starch paste when subjected to low temperatures, preferably about 20° C. A spongy mass results, the individual particles of which show distinctly a fibrous structure to such an extent that when it was first observed it was seriously

proposed as a material for paper making, wood pulp being then still unknown. Once fairly dry, no paste can be made of this starch derivative. Within the same category must also be classified the so-called reversion products of starch, the formation of which can be observed in solutions of normal or soluble starch when left standing for some time. The deposits which form cannot be brought in solution again. The starch cellulose isolated by mægeli from starch belongs likewise to this class.

The one particular kind of modified starch belonging to this group to which it is desired to call particular attention is the so-called "non-gelatinizable" starch covered by U. S. Patent No. 982673, issued January 24, 1911. This form of starch perhaps more than any other illustrates the extreme lability of the complex starch grain, because the change in this instance is brought about in a cold and fairly neutral medium, and under conditions which would seem to preclude any far-reaching destructive reaction on the starch molecule itself. This form of starch is easily prepared by bringing starch in contact with a comparatively weak solution (5%—10%) of formaldehyde containing sufficient of an ammonium salt of the heavy acids to form hexamethylen tetramine. The contact should continue for a few hours, the mixture being stirred but not heated. It will be found that, as the time of contact increases, the starch when removed from the mixture and boiled with water becomes less and less gelatinizable and that after the reaction has been completed no trace of gelatinization will be noticeable, but that on the contrary the starch so prepared will—even after prolonged boiling with water—remain absolutely unaffected and sinks to the bottom of the test tube, as any other insoluble powder would. When this point is reached, the starch is separated from the liquid and washed until no reaction is shown in the washing water for either formaldehyde or ammonium salt. As indicated by its name, this peculiar form of starch is characterized by its inability to gelatinize with water on boiling, in fact, if the washing has been complete, a point will be reached when the water having been boiled with the starch will not show any coloration with iodine, although the prepared starch itself, when moistened with iodine solution, will become intensely blue. This form of starch remains unacted upon not only by waters but

relatively strong boiling solutions of caustic alkalies are without effect on it, and it was possible to introduce acetyl and benzol-radicals into the molecule without any outward change in appearance having been noticed. Mineral acids, on the other hand and also some of the stronger organic acids like oxalic, seem to affect this ungelatinizable starch even more nearly than ordinary starch forming dextrose, though the transition through the dextrin form is noticeable and through that of maltose probable.

The mechanism of the formation of this form of starch is interesting. Formaldehyde alone will not accomplish it, still less hexamethylen tetramine. A mixture of formaldehyde and an acid will bring about the desired result to some extent but it must be a strong mineral acid, hydrochloric, sulphuric and nitric acids, in the order given, being available. But with acids alone, a relatively strong solution must be used, while if the corresponding ammonium salt is employed the quantity required is considerably smaller. With a proper mixture of formaldehyde and ammonium salt, it is also possible by the same treatment to render soluble starch, prepared by the Lintner or any other method, entirely insoluble and ungelatinizable, and under certain conditions even the dextrins will show the same result.

There is much reason for the statement and little to the contrary that the reaction described above does not affect in the least the chemical composition of the starch, but merely extends to the surface of the starch granule, hardening it and making it insoluble in the same way as the formaldehyde reacts upon gelatin and other nitrogenous organic colloids, although in this instance the necessary presence of an acid or still better of an ammonium salt as a contact substance, or catalyzer, is interesting. The colloidal character of the reaction is undeniable. This non-gelatinizable starch retains traces of formaldehyde very tenaciously even after prolonged washing as distillation with acids show.

RESOURCES AND CONDITIONS IN THE STATE OF WASHINGTON FOR PAPER MAKING

By Guy C. Howard
Everett, Washington

INTRODUCTION

The scope of this paper is to present some general information regarding the resources and conditions which exist in the State of Washington affecting the question of the development of paper-making and allied industries. Features of the situation will be taken up which would naturally be of interest to parties anticipating the investment of capital in the development of these industries, but details regarding the technology and commercial phases of any particular line of paper making will not be gone into, as these are from necessity a matter of detailed investigation preliminary to actual investment. The resources of the State are such as to invite development, and paper making will be one of the leading industries of the future, but to insure this development taking place so as to result in the most permanent and lasting benefits it must be carried on along natural and reasonable lines and with a full knowledge of conditions as they exist. It is to be desired that this paper may be the means of bringing the resources of the State to the favorable attention of those interested in the paper industry and at the same time give some idea of the situation as regards markets, manufacturing costs and investment required.

RAW MATERIALS

Woods of various kinds exist throughout the State in abundance. Spruce, hemlock, fir and cottonwood are principally confined to western Washington, while pine predominates in the eastern part of the State. All of these species are being used at present to make paper of various grades. The slabs, edgings and sawdust from the extensive lumber industries of the State f r ish an enormous quantity of material of prospective value,

and particularly for special grades not now being made. The grain regions of the central and eastern portion of the state provide a very large tonnage of straws.

These raw materials exist in ample quantity to support an extensive development of the industry. In general they are easily accessible to transportation and power, but this is not true in the case of cottonwood, which is of particular value in book and magazine papers. The manufacturers in this line are already confronted with the necessity for reforesting to assure a future supply of this species.

POWER RESOURCES

The water power development in the State is only in its infancy. Many power sites exist of which some have already been developed on an extensive scale. The State as a whole, and particularly the region west of the Cascade Mountains — known locally as western Washington — is destined without question to be a region of cheap and abundant power. Ample evidence of this fact is apparent on every hand. Conditions are such, however, as to lead to the development of this power in large projects for the commercial sale of power rather than in the line of small individual power sites.

Fuels for steam power are available in abundance and in several forms. The extensive oil fields of California and the easy means of transportation by tank steamer make oil a cheap and reliable fuel supply. Enormous quantities are consumed at present for power plant and locomotive use. The coals mined in the state are available to a limited extent for power purposes and can be gotten in grades from a good bituminous down to a lignite. The Alaska coal fields when opened up and developed, will be easily accessible to the state and assure a permanent and cheap fuel supply. The wood refuse from the saw mill industry, under favorable conditions of equipment to handle, provides a very cheap fuel for certain locations.

MARKET CONDITIONS

The question of a market for a manufactured product as paper is one easily overlooked, and especially so in developing an industry remote from congested population. It is of course a matter

of the most vital importance. With the present freight rates
the market accessible to paper made in Washington, in equal com-
petition with Eastern mills, comprises the States of Washington,
Oregon, California, Idaho, Utah and Nevada. The last census
report gave Washington a population of a little over one million
people, and showed the combined population of the above named
states to be approximately five million people. This amounts
to but about five per cent of the total population of the United
States. This population is increasing rapidly and undoubtedly
will continue to do so, still as compared with conditions in the
Atlantic Coast States, the home market for an industry in this
region has distinct limitations. Furthermore, in most grades of
paper made in this section the disposition of the manufacturer
is to keep pace with the increase in home consumption by an
increase in his capacity, which is a natural thing to do, as in gen-
eral the plants are small. A home market that will absorb at
least 65% of a paper plant capacity is essential to success in this
region as in most others, and the more nearly the full capacity
output can be marketed in home territory the better the position
of the manufacturer.

As regards export trade, the experience of the manufacturers
here has been that they cannot at present compete on price in
the world markets. This is a condition which will improve as
time goes on, but at present the state is a region of cheap raw
materials and cheap power, but one of high cost for labor, supplies
and equipment, and consequently high investment per ton of
production. In competition with the world in export trade the
disadvantages of the latter items more than offsets the advan-
tages of the former, so the cost of production is distinctly higher
in the West than in Eastern and European mills.

The opening of the Panama Canal will be a factor destined
ultimately to favor the paper industries of Washington, but the im-
mediate effect will be to the advantage of Eastern mills. The
present selling price of paper on the Pacific Coast is based on the
selling price in the Eastern market plus the freight to Pacific
Coast points. The freight differential now amounts to $15.00
per ton, but with the opening of the canal this will be reduced
to $9.00 per ton or less, so the Washington manufacturer

will be confronted with an immediate reduction of at least $6.00 per ton in the selling price of his product. This reduction must be offset by a reduction in his manufacturing costs, and while the reduced freight from eastern points will lower somewhat the cost of his chemicals, supplies and repair equipment, still it will not make him any nearer the base of supplies in these items, nor reduce the necessity of his carrying large stocks to prevent loss through shut down. The opening of the canal will of course afford a cheap and direct transportation to Atlantic Coast points, but this will only be of advantage to the Washington manufacturer when an increase in cost of raw materials or labor costs in the East establishes a balance so the advantage of cheap raw material and power in Washington more than offsets cheaper cost of labor, supplies and equipment in the East. This will come ultimately but the Washington paper manufacturer can hardly expect to compete on Atlantic Coast points for some years to come. The increase in the population of Washington due to direct European immigration will be a distinct factor in the growth of the western home market.

LABOR

The cost of all kinds of labor in Washington is 33% or more higher than in the East and the direct bearing of this is an increase in manufacturing cost of production. Any change in this labor situation will be gradual at best and only on certain classes of unskilled labor affected by direct immigration from Europe through the Panama Canal can any reduction on the present scale be looked for. A reduction in the difference between labor cost in the Eastern and the Western mill is more likely to come from an increase in cost of skilled labor in the East rather than a lowering of present wages in the West on this class of labor.

EQUIPMENT AND SUPPLIES

Most of the equipment and supplies used in the paper industry come from the East or Europe, which means a materially higher cost to the Washington manufacturer on chemicals, wires, stones, fillers, repair parts, and initial equipment. This location of a plant two or three thousand miles from a base of supply ne-

cessitates keeping a much larger stock of supplies and repair parts on hand at all times to safeguard against shut down. Both the above items are factors in the cost of production and must be taken account of by the Washington manufacturer.

PRESENT INDUSTRIES

The following named plants are already operating in the region that would be a " home " market for a Washington manufacturer, and give some idea of the situation as regards competition in the various kinds of products:

Everett Pulp & Paper Co., Everett, Washington. Book, magazine and chemical writing.

Willamette Pulp & Paper Co., Oregon City, Oregon. News.

Crown Columbia Pulp & Paper Co., mills at Camas, Wash., Oregon City, Oregon. News, wrapper, fruit tissue.

Hawley Pulp & Paper Co., Oregon City, Oregon. News and fruit tissue.

Lebanon Paper Co., Lebanon, Ore. News and wrapper.

Inland Empire Paper Co., Spokane, Wash. News and fruit tissue.

Floriston Pulp & Paper Co., Floriston, California. News and fruit tissue.

Pacific Paper & Boxboard Co., Seattle, Wash. Boxboards.

California Paper & Board Mills, Antioch, California. Boxboards and sheathing paper.

LINES FOR DEVELOPMENT

On the grades of paper already manufactured here further development should be a result of careful investigation, in view principally of the present limitations of the home market. In some lines the field will be found amply covered, in others opportunity may exist for new plants. On lines not already manufactured here the field is a promising one.

The particular resource that invites development and use is the waste from the lumber industry in the form of sawdust, slabs and edgings. With the present cost of cord wood for pulp it is not economical to use sawmill slabs to make into white stocks owing to the high cost of perfectly cleaning and freeing from bark.

Neither is the wood resinous enough to work for turpentine by the steam process as practised in the long leaf pine region of the South.   There is, however, a large amount of this waste that can be easily segregated to give a raw material sufficiently clean and of good fibre length for many purposes.

CONCLUSION

In conclusion it may be justly said that the State of Washington has abundant raw materials and ample cheap power, both steam and water, to maintain an extensive development of the paper industries.   The determining factors in the success of plants making any grade of products is the present limitations of the home market and the higher manufacturing cost per ton of output than in Eastern mills, both of which items are becoming more favorable from year to year.   In several grades of products not being manufactured at present, an attractive opportunity exists for immediate investment and the whole field warrants investigation, as the State is destined to be known as one of extensive paper industries.

THE INFLUENCE OF BY-PRODUCTS UPON THE DEVELOPMENT OF THE INDUSTRY OF CORN PRODUCTS

By H. C. Humphrey
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The manufacture from the kernel of corn (Zea Mays) of the various products which are now exploited has been of slow growth. The first attempt to produce starch from corn was made by Thomas Kingsford, who after several years' discouraging experiments, succeeded in making corn starch of excellent quality, both for edible and laundry purposes, and established in 1848 the first corn starch works at Oswego, N. Y.

In order to clearly understand the problems which have had to be solved in the manufacture of corn products, and to follow historically the steps which have been taken in the utilization of every portion of the kernel, the following diagram has been prepared, which shows the constitution of the corn kernel and the comparative development.
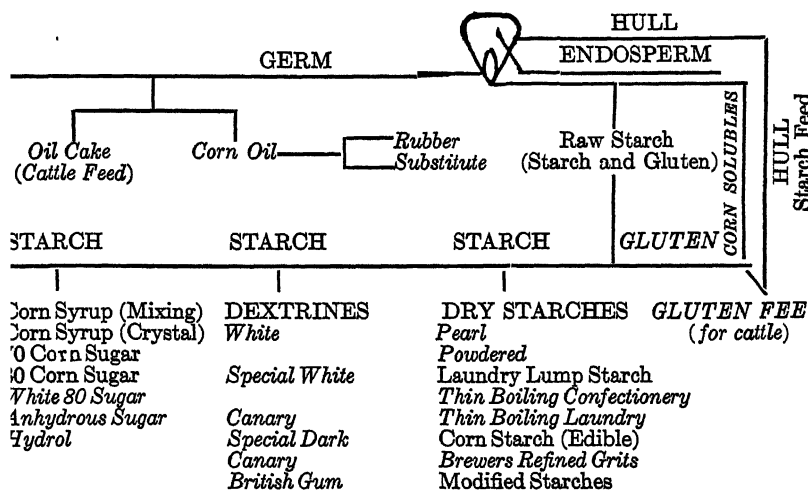
Roman — Products made before 1881.
Italics — Products made after 1881.

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It is not the object of the present paper to enter into the details of manufacture, but simply to point out the influence of the utilization of by-products on the development of this important American industry, I will briefly describe the process so that the matter may be clearly understood.

As the aim of the early manufacturer was to produce starch alone, it was only necessary to soften the grain by steeping in warm water or water to which a small amount of alkali was added, whereby an incipient putrefaction of the germ and nitrogenous substance was engendered, and then by grinding and sieving to separate the hull and part of the germ from the endosperm. The ground germ and hull was found to be excellent cattle feed, and until 1881 sold in a wet state under the name of "starch feed." The endosperm, which contains the starch and gluten, was then, by a process of washing, in which alkali and water were employed, and of settling and decantation, or by running over the so-called tables, separated into starch and gluten. The gluten was for the most part wasted. The starch was then either dried and made into laundry and edible products, or transformed into corn syrup (glucose) or corn sugar (grape sugar).

The modern process of corn starch manufacture was developed, through the labors of Dr. Arno Behr, and the author working partially along lines, first suggested by Chiozza, in which sulphur dioxide was employed in the steeping of the grain. Through the efforts of Messrs. F. O. and E. A. Matthiessen, this process was first established in 1881 at the Chicago Sugar Refining Company.

By this process the corn is softened in warm water to which a trace of sulphur dioxide is added. The sulphur dioxide not only prevents during the steeping the decomposition of the germ and gluten, but partially dissolves the intercellular tissues, thus rendering the component parts more easily separated by the subsequent operation. The softened corn to which water has been added is crushed in a mill, so constructed that little injury is caused to the elastic germ. The mass is then run into long tanks provided with appropriate conveyors and skimming apparatus, filled with starch liquor of about 8° Baume. The germs, containing a large amount of oil float to the top and are run over sieves. The hulls being heavier, sink to the bottom and are carried over sieves. The germs and hulls are thus respectively separated from the starch

liquor, made up of crushed endosperm (gluten and starch). This latter is now separated as in the older method, by running over the tables.

In 1881, the gluten, which was formerly run to waste, except occasionally, when it was carried off by the farmers in barrels and fed to the stock, was for the first time recovered in a dry form by a method consisting of filter pressing, drying and grinding. A few years after the hulls, which had been sold in the wet form, were incorporated with the gluten, dried and ground, thus constituting gluten feed.

In 1893-1894, the corn solubles, contained in the water in which the corn had been steeped, were first concentrated and mixed with the gluten feed. At this time only about one-half of the solubles of the corn were recovered, the portion remaining in the steeped corn after the removal of the steep water being lost by washing in the subsequent processes. In 1908, there was introduced a continuous diffusion system, whereby the corn solubles were concentrated in the steeping, and as a result an additional amount of dry corn solubles was saved.

A stage in the development of this industry has now been reached where practically all of the original raw material is recovered; any future advance must be, therefore, in modifying the products or extracting from them materials which are better fitted for some special use in the arts, and, therefore, commercially of greater value. A new modified form of starch, as described in U. S. Patent No. 855,599, is an apt illustration of work that is being done along these lines. However, corn solubles appear to present the most promising field in this respect. They are now incorporated with the gluten feed. In order to afford an insight into the possible uses for which this material is fitted, the following average analysis of corn solubles on a dry basis is here given:

N x 6.25	40.00%
Reducing Sugar, as Glucose	25.00%
Phosphoric Acid (P_2O_5) Organic (Phytin)	4.80%
Phosphoric Acid (P_2O_5) Inorganic	2.50%
Sulphuric Acid (SO_3) Combined	1.66%
Hydrochloric Acid (HCL) Combined	.54%
Calcium Oxide (CaO)	1.00%
Magnesium Oxide (MgO)	2.71%

Potassium Oxide (K$_2$O)	5.76%
Sodium Oxide (Na$_2$O)	1.12%
Acidity (Phenopthalein as Indicator)	181. CCSN/L
	NaOH to 100 gms.
Alkalinity (Methyl Orange as Indicator)	55 CCSN/L
	HCL to 100 gms.

The 40% of nitrogenous material calculated as protein is in the form of amino and other compounds, resulting from the cleavage of the protein during the process.   These non-protein bodies, according to the latest nutrition investigations, are of much greater value than was formerly supposed, being now shown to be equal to protein in "maintenance," although not in "production."

The organic phosphorous compounds have not as yet been closely studied, but are doubtless similar to the phytin of other grains.

The following possible commercial uses for these corn solubles have been suggested: As a fertilizer, the contents of 7.65 NH$_3$ 6.8%, P$_2$O$_{10}$ and K$_2$O gives it a fertilizing value of a little less than is now obtained for it in its present form as a cattle feed.

As a yeast food, preliminary experiments have already been made, which seem to show that it is of substantial value to the fermentation industries.   It may also find use in the manufacture of compressed yeast.

As a food, corn solubles mixed with corn syrup may be made into a refreshing beverage.   The amino compounds, as well as the possible therapeutic value of the organic compound, may add to its nutrition value.

Appetizing soups have been prepared.   These resemble the vegetable extracts which are now being made from yeast and various vegetables and grains, and are found on the market alone or or mixed with beef extracts.

These are some of the possible uses which in the future may be found for this by-product, and as there are about 100,000,000 pounds of dry corn solubles produced yearly, the importance of this subject is evident.

Previous to 1881, the products obtained were starch and starch feed, and it is safe to say that their total yield from corn (dry basis)

was not more than 70 to 75%. The large amount of valuable material thus wasted, which consisted of gluten and corn soluble, and a part of the germ, being in its nature highly nitrogenous, was very putrescible, and grossly polluted the streams into which it flowed, and gave rise to complaints and many law-suits. The plants were necessarily built of moderate size and mostly in small towns, therefore it was impossible to reap the economical advantages possessed by the centrally located factories of today.

Formerly the price of corn was so low that it was possible to obtain satisfactory returns on the investment even when 25% to 30% of the raw material was wasted. Of late years conditions have greatly changed. Corn has advanced in price and doubtless will continue to do so. It is estimated that of the annual corn crop of about 3,000,000,000 bushels, 85% to 90% are fed on the farm, being transformed into cattle, hogs, poultry, milk, butter and eggs, and as these latter provisions are yearly increasing in price, there seems a strong probability that in the future the farmer will sell less and that there will be a gradual increase in the value of the marketed corn.

On the other hand, the price obtained for the products, starch, corn syrup, corn sugar, is to a certain extent limited by the price of their natural competitors, which are starch and glucose from the potato, sago cassave and other starch producing plants, and sugar, syrup and molasses from the cane and beet.

In order to conduct the business on a profitable basis it is necessary to conduct it on a very large scale. For instance, a factory recently erected has a daily capacity of 45,000 bushels of corn, therefore the location must be where there is a central grain market of sufficient size to furnish daily such an amount of raw material. Again it must be located where the lowest freight rates can be had, where the shipping facilities are the most favorable and labor the cheapest. Besides these advantages of location, the process must be conducted and controlled by the most modern mechanical and chemical methods. Yet with all this care and vigilance, the corn starch industry could not exist today were it not that the by-products had been utilized to the fullest extent, for the present cost of corn is nearly as great as the price obtainable from the recovered starch and starch feed, had no other by-products been saved.

COMMERCIAL CELLULOSE CHEMISTRY, PARTICULARLY RELATING TO CELLULOSE ACETATE

By Harry S. Mork
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Although the title of this paper is exceedingly comprehensive, it should be explained as a preliminary that, while it is intended to cover in a general way some of the points and problems embraced by the broad subject, it is the intention chiefly to cover more in detail that special corner of cellulose chemistry which has received much attention during the past decade, but which has been especially the subject of highly active industrial research during the past five years, both in America and Europe; in other words, the cellulose esters of organic acids, particularly cellulose acetate.

The literature on cellulose and its chemistry is far from being voluminous, although it has had two distinct contributions in the past two or three years in Worden's "Nitrocellulose Industry" and Schwalbe's "Die Chemie der Cellulose." Why there has not been more intimate study of the subject with more recorded data is not difficult to answer. Primarily, notwithstanding that cellulose, as the chief component of cotton, or flax, or hemp, or wood, and in fact all forms of plant life, is scattered over the face of the earth in the greatest profusion and abundance and is of the most fundamental importance to the well-being of human life, the study of its composition and reactions is really a small and highly specialized branch of the great science of chemistry. This is no reason for neglect, if the study of cellulose has indeed really been neglected, but if we stop to think of the reactive inertness of cellulose, of the great complexity of aggregates of this type, and of our deficiency of knowledge of the fundamental laws governing the behavior of such complexes, and when in addition in this particular case we also consider that the synthesis of cellulose offers no inducements to the pure chemist, it is not to be wondered at that more effort has not been concentrated on

the study of the ultimate composition of cellulose, or of its exact structure. As might be expected, there has been much conjecture, much theorizing and in consequence much controversy over what the probable structural formula of cellulose might be, but the opinion is here voiced without hesitation, although others may perhaps have previously expressed it, that the available data at present is all too insufficient to justify· even a serious assumption of the probable chemical structural make-up of cellulose.

Now cellulose is a material of the first order for technical application, and while it is impossible to say to what degree the deficiency of composition data has retarded its industrial developments, it is nevertheless true that nearly every known chemical reaction in which cellulose participates has been practically utilized with much profit and benefit to the community. Realization of this fact has at last come to chemists, and the technical cellulose field is now being explored with really remarkable endeavor.

Several known facts of first importance should be borne in mind and they are here referred to because they are pertinent to cellulose chemistry in its broad aspect, and because they have particular bearing on the proper understanding of the physical and chemical properties of the cellulose esters. These facts are: first, that cellulose is a molecular aggregate of high complexity, and in consequence can pass through various reactions with the possibility of producing an indefinite number of products of like empirical composition, but varying in the degree of aggregation and, therefore, in physical properties; second, that cellulose as such is not soluble in neutral solvents, and either acids or alkalies, so far as we now know, must be present in the different reactions in which cellulose participates; third, that all cellulose reactions seem to require, or are accompanied by, either hydration or hydrolysis, prior to, during or subsequent to, the general reaction.

To the first of these facts, complexity of the cellulose molecule, can be attributed the now firmly established precedent, that a very long period of experimental development must be expected to ensue between the discovery of a new cellulose reaction and the time when it shall be sufficiently perfected to be considered a positively demonstrated practical application, pro-

vided of course that the reaction is of that class which permits of such development and application.

Through just such a trying period has passed the nitration of the cellulose, and the formation of viscose, or cellulose xanthogenate. From a like period the acetylation of cellulose has not yet wholly emerged, but now, forty-three years after Schutzenberger recorded his experiment of producing cellulose acetate by heating cotton cellulose with acetic anhydride in a sealed tube, and nearly twenty years after Cross and Bevan utilized the more reactive recovered cellulose from their viscose process as the cellulose base for acetylating, now indeed has the perfected present-day cellulose acetate become a controllable industrial material with not only its limitations but its great possibilities well recognized.

As has been stated, that cellulose could be acetylated has been known for nearly fifty years, but the real father of the modern cellulose acetate industry is A. P. N. Franchimont, who found, and publicly disclosed in various scientific journals about thirty years ago and later, that cellulose could be acetylated by acetic anhydride with great facility provided a small amount of sulphuric acid was added to the reaction mixture, and who, moreover, showed that the quantity of sulphuric acid and the conditions of the reaction influenced the physical properties of the cellulose acetate produced.

Nowadays all cellulose acetate is made by this general method of adding an assisting or condensing agent to the reaction mixture consisting of cellulose, or modified cellulose, and acetic anhydride, and the different patented processes vary either in the form of cellulose used, the nature and quantity of the condensing agent, the general reaction conditions of time and temperature and the method of recovery of the acetylated cellulose. With the exception of the Cross and Bevan acetylation method of acting on recovered cellulose from viscose by means of acetyl chloride and an inorganic acetate, essentially all the contributions to the patent literature on cellulose acetate covering the manufacture of this product have been issued subsequent to 1899, and they all follow the general basic method of Franchimont, and must therefore be interpreted as being valid within the limi-

tations of the conditions specified, but provided of course that these conditions are true in fact, and not previously anticipated.

When cellulose is acetylated, using of necessity acetic anhydride and diluting if necessary with acetic acid, the cellulose acetate passes into solution as fast as formed and is recovered from the solution in a powdery, granular or horny mass by precipitation with water or some other non-solvent of the ester such as a hydrocarbon or carbon tetrachloride.

Prior to about seven years ago the granular, amorphous form of cellulose acetate was the only variety known, but about 1905 it was learned that the acetylation could be conducted in a bath in which the ester was insoluble, and the product so produced retained the general physical form of the initial cellulosic material, so that if cotton yarn is used, the end product is cellulose acetate yarn.

A process of this character has positive inventive features which are obvious and which do not pertain to any of the other processes, such as producing acetylated celluloses of fibrous or other specific forms, and the ease of solubility, but it has also other advantages which are not obvious. Among these are ease of control, with the possibility of standardization of products, practically theoretical yield, and the ability to retain the molecular aggregation of the cellulose to a far higher degree than seems to be possible by any of the solution processes. This last is of fundamental importance because the degree of aggregation primarily determines the strength of the commercial products which can be made from the cellulose acetate.

On this account, if for no other, it is believed that the cellulose acetate of the future will all be made by the fibrous method. Fortunately a relative measure of the aggregation is to be had in the viscosity of solutions of cellulose acetate in a standardized solvent.

Cellulose compounds in general show so many solubility-peculiarities and possible property-variations that it is not to be expected that the acetylation of cellulose is by any means a simpler procedure than nitration for instance. Speaking particularly of the fibrous acetylation of cellulose, it requires careful adjustment of the proportions of reagents, of the time and tem-

perature conditions and of the character of the original cotton to be acetylated in order to secure the maximum control of product which the process affords.

Referring entirely now to the process of preparing fibrous cellulose acetate in a high degree of aggregation, — in the first place the cotton cellulose to be acetylated must be carefully prepared and not structurally weakened by the cleansing or bleaching process. This high grade cellulose is then subjected to a preliminary treatment with acetic acid, water and a condensing agent, as for example sulphuric acid, under particular conditions whereby, as far as we now know, the cellulose is hydrolized so that one molecule of water is added for every thirty-six atoms of carbon, or for every six groups of the formula representing the empirical composition of cellulose as follows:

$$(C_6H_{10}O_5)_6 \ . \ H_2O$$
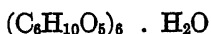
This initial hydrolysis seems to be essential for a controllable acetylation, and the conditions of the hydrolysis are vitally important. After the preliminary treatment, the excess of reagents is removed mechanically and the acetylation proper takes place in a bath consisting of acetic anhydride and a restraining agent, usually benzol, but the bath otherwise modified in a way which technical experience has demonstrated as being advantageous for producing the best quality of cellulose acetate. The temperature is carefully controlled throughout the acetylation, and all the other conditions are adjusted from start to finish, so that the end product shall be cellulose triacetate of desired solubility and viscosity. Compared with most chemical reactions, the process is a slow one, for it is rarely complete inside of eight hours, but best results are not usually obtained by an acetylation which takes much less than eighteen hours. The reaction proceeds so slowly that at any time during its course a small sample can be removed and tested to see if it meets specification. When the acetylation is complete, the mixture of acetic acid and benzol is drained from the cellulose acetate, which is thoroughly washed free from acid and dried and the acetic acid and benzol can be separately recovered by distillation or otherwise and utilized again. During acetylation, the fibre bulks up greatly, which is

to be expected when it is realized that the original cotton increases approximately 75 per cent in weight in its conversion into cellulose triacetate. Theoretically, 100 parts of dry cellulose should yield 178 parts of cellulose triacetate, and in a properly conducted fibrous [acetylation practically this yield is regularly obtained. It used to be considered at one time that ordinary acetylated cellulose was tetracetate of cellulose, but now it is generally conceded that the maximum degree of acetylation obtainable corresponds to cellulose triacetate. The mistake has been in part due to saponification methods. By boiling with half-normal alcoholic potash solution, saponification values are frequently obtained which correspond fairly closely with calculated figures for cellulose tetracetate, due undoubtedly to further decomposition of the cellulose by the alkali. With half-normal alcoholic potash diluted with an equal volume of water, true values are obtained after one to two hours boiling. This seems to be a rapid and accurate method.

A point is here recorded as being of interest in the pure study of cellulose chemistry. It does not seem possible to acetylate cellulose directly by acetic anhydride alone without a condensing agent, except at very high temperature, and then there is some question whether at these temperatures the cellulose is not subjected to partial decomposition whereby the reaction is enabled to take place. This occasions some doubt as to whether there are in normal cellulose any free hydroxyl groups, which uncertainty is by no means clarified by the observation that cellulose recovered from cellulose triacetate by saponification does not seem to be any more easily acetylated by acetic anhydride alone than is the original cellulose.

As nearly all the practical applications of cellulose acetate require it to be either gelatinized or dissolved, the solvents of cellulose triacetate are a matter of primary consideration. These solvents are not generally the same as those of cellulose nitrate and there are relatively few in common. In the main, the chief solvents of cellulose acetate are of two classes, — chlorine compounds and phenols. There are a number of other solvents outside these classes along which is acetone. The question of acetone solubility[will be taken up now because it introduces another

peculiarity of cellulose acetate. If the acetylation is brought about by a relatively small percentage of condensing agent, as for example sulphuric acid, the cellulose acetate produced thereby will be only slightly, if at all, soluble in acetone; if the percentage of sulphuric acid is increased, the solubility in acetone is increased. Better yet, if after the cellulose acetate has been formed it is digested for some time with aqueous solutions of mineral acids of moderate strength, it will become entirely soluble in acetone. Because, after acetylation, the cellulose acetate is always immersed in water to free it from the acids used, the above described after-treatment always takes place in the practical manufacture of cellulose acetate, and because it takes place more rapidly when the aqueous acid is stronger, accounts in a great degree for the fact that cellulose acetates prepared with a larger percentage of condensing acid show greater acetone solubility than those prepared with only a relatively small amount. The change to acetone solubility has been inferred to be occasioned by hydration or hydrolysis of the ester, but no concrete data has as yet been advanced to verify this inference. This is true, however, that the acetone soluble cellulose acetate shows a wider range of solubility in other solvents than does the kind not soluble in acetone.

Returning now to the two general solvent classes previously mentioned; of the chlorine compounds, chloroform and tetrachlorethane or acetylene tetrachloride are the most important, the latter being a much more powerful solvent than chloroform. Methylene chloride, ethylene chloride, epichlorhydrine, dichlorhydrine, methyl chloracetate, ethylenechlorhydrine, acetochlorhydrine, ethyleneacetochlorhydrine, dichlorethylene, trichlorethylene are some of the other chlorine solvents of varying degrees of solvent power, some of them only solvents of the acetone soluble acetate and some only exercising solvent power in the presence of limited quantities of methyl and ethyl alcohols. Neither methyl nor ethyl alcohol is, strictly speaking, a solvent of cellulose acetate, but these alcohols added to most of the chlorine solvents increase marvelously the solvent power of the solvents, creating in some of them general solubility where otherwise it is limited to certain kind of cellulose acetate, and causing in the case of others marked decreases in the viscosity of the

solutions, with the possibility of producing flowable solutions of high concentrations. The viscosity reductions are, however, not so great with ethyl alcohol as with methyl alcohol.

Phenol, or carbolic acid, is perhaps the most powerful of all the solvents of cellulose acetate, but other phenols like cresol, thymol, guaiacol, carvacrol, benzyl phenol, amyl phenol, and resorcin are also excellent solvents. One measure of the solvent power of a phenol is the degree to which a given cellulose acetate solution in it can be diluted with benzol without causing permanent coagulation. Most peculiarly, ethyl or methyl alcohol cannot be added to phenol solutions of cellulose acetate to anywhere near the extent that benzol or its lower homologues can be added.

Of some of the other fairly strong solvents mention might perhaps be made of formic acid, acetic acid, pyridine, aniline, methyl formate, methyl lactate and methyl and ethyl acetoacetate. There are also perhaps a few solvents of very limited solvent power like diacetone alcohol and methyl and ethyl acetates. Amyl acetate and ether alcohol mixtures, ordinary solvents of cellulose nitrate, are not solvents of cellulose acetate.

It is not the intention of this paper to discuss at any great length the commercial applications of cellulose acetate, and yet perhaps a few words on this branch of the subject may be of interest at this time. Cellulose acetate is essentially adaptable for the manufacture of all the products for which cellulose nitrate can be used, except of course explosives, and because the acetate is so slowly combustible it has even a much larger field of usefulness. Many of these uses are now in the course of technical development, coincident with which is a gradual lessening of the cost of production.

It will not be very long before the highly inflammable and hazardous celluloid moving picture film will be entirely replaced by the safe cellulose acetate film. A step has been made already in this substitution, and were it not perhaps for unpreparedness and monopolistic suppression, the substitution would be complete by now.

As an effective insulation of very fine wire, cellulose acetate has been technically applied for over ten years, having certain mechanical advantages possessed besides only by cellulose nitrate,

but having the additional virtue of far greater stability and permanence at much higher temperatures. For the manufacture of waterproof artificial silk and imitation bristles, cellulose acetate is unique. The nitrate is not at all suitable for these purposes because of its hazardous inflammability in the necessarily fine state of division of the material in these applications, and if the inflammability is removed by denitration all the waterproof properties are also lost. For the manufacture of ready mixed bronze and gold paints, a cellulose acetate solution in acetone is peculiarly suitable, while cellulose nitrate solutions are not, particularly because the latter corrodes bronze powder, while the former does not. Again, for waterproofing aeroplane cloths and imparting rigidity, cellulose acetate is well adapted, while the nitrate is too hazardous to use. It is expected that ultimately cellulose acetate will substitute effectively for many of the present applications of celluloid, but it is not intended by any means to convey the impression that celluloid will ever be completely eliminated, for it certainly has many uses for which cellulose acetate cannot be adapted, just as there are many more applications than have been mentioned in which cellulose acetate products will have a distinct field of their own.

THE OCCURRENCE OF PENTOSANS AND HYDRO-
LYZED PENTOSANS IN CORN (MAIZE)
AND CORN PRODUCTS

By Christian E. G. Porst
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The chemical laboratories in the factories which manufacture corn products control the daily work by a number of tests—starch, protein, fat, etc.—in intermediate as well as in finished products, but hitherto little or no attention has been paid to the pentosans.

It is the purpose of this paper to trace the pentosans from the corn kernel through the various products of disintegration down to the finished products, to see to what extent they are present.

Therefore I will have to outline the process of disintegration but shall do that as briefly as possible and refer readers who want further information to a more thorough description of the American industry of corn products which has been given by T. B. Wagner in the *Journal of the Society of Chemical Industry*, Vol. XXVIII, 1909, No. 7.

I have used in my work Councler, Tollens and Krüger's phloroglucin method for the determination of total pentosans, Votocek, Tollens and Ellet's alcohol extraction for the determination of the methyl pentosans. Results are given according to the tables calculated by Tollens, Kröber and, Ellet and for, the sake of uniformity and comparison, all results are given as pentosans and methyl pentosans figured on dry basis.

The method requires that the phloroglucin added for precipitation shall be twice the amount of furfural expected; therefore I have made preliminary tests for each individual group of material, using an excess of phloroglucin, but otherwise the results were not considered. Where determinations were made in products with excessive moisture, the first portion of hydrochloric acid added was stronger than the 1.06 sp. gravity prescribed in the method and then of such calculated strength that the right gravity was obtained.

To avoid any oxidation of the phloroglucid, large glass-stoppered weighing bottles were used to place the Gooch crucibles in while cooling in desiccator and weighing.

A number of determinations were made, but, the corn excepted, only the average results are given here. As it is interesting to see in what proportion to each other pentosans and methyl pentosans are present, this relation has been figured out as parts in 100 parts total pentosans for each of the various products.

1. *Corn.*

Pentosan	Methyl Pentosan	Moisture	Dry Basis Pentosan	Methyl Pentosan	Total
4.38	.536	19.50	5.44	.666	6.106
4.69	.780	18.50	5.75	.957	6.707
4.95	.750	18.50	6.08	.920	7.000
4.54	.780	19.76	5.66	.972	6.632
4.77	.420	19.60	5.93	.522	6.452
Average					
4.67	.653	19.17	5.77	.808	6.578

100 parts pentosan in the corn kernel consist of 87.72 parts pentosan and 12.28 parts methyl pentosan.

Botanically seen, the corn kernel is a one-seeded, dry, indehiscent fruit (caryopsis). Pericarp and testa grow together forming the hulls. Inside the hulls is endosperm and embryo. The former consists of parenchym cells containing starch granules or starch and gluten granules together and in its periphery one single layer of cells: the enzyme cells (aleurone cells).

The enzyme cells do not contain starch but chiefly fat and protein. They cover that part of the endosperm which contains "horny starch."

On the upper side of the corn kernel, between hulls and endosperm and submerged in this latter we find the embryo (germ) consisting of the large scutellum with embryo root, stem and bud.

The grade of corn used generally in the corn products industry consists of

2.   6.8% hulls
                85.7% endosperm
                7.5% germ.

80 SUGAR.

23% SOLUTION IN ½"CELL, LOVIBOND'S COLORIMETER

ORDINATES = LOVIBOND TINT UNITS
ABSCISSAS = NUMBER OF DAYS
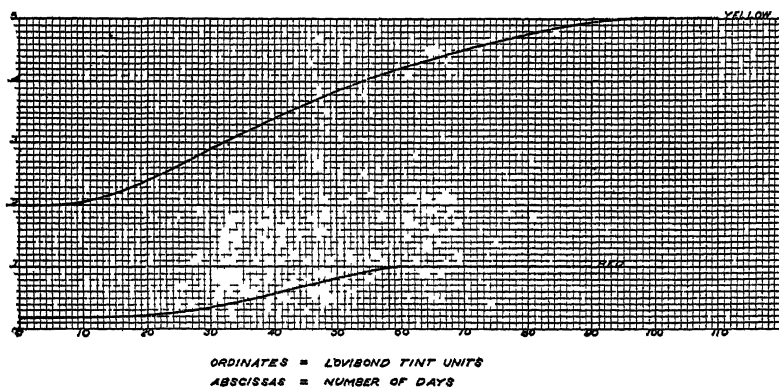
To test what amount of pentosans these various component parts of the corn contained, a disintegration was made in the following way: Corn was steeped in boiling water for a few seconds, then hulls and germ were easily removed from the endosperm with a penknife.

I tried to separate the enzyme cells from the rest of the endosperm but did not succeed in getting a clean preparation, as it was impossible to skin off this layer of cells without getting some of the starchy endosperm removed too. Instead I made a preparation of endosperm from which all of the enzyme cells were removed.

These four preparations gave the following results:

	Pentosan	Methyl Pentosan	Tptal	100 parts Pentosan consist of	
				Pentosan	Methyl Pentosan
Hulls	48 620%	6 040%	54.660%	88 95	11.05
Endosperm	1 690%	867%	2.557%	66 09	33 91
Endosperm minu. enzyme cells	422%	1 130%	1 552%	27.19	72.81
Germ	8.382%	.231%	8.613%	97.32	2.68

From the above data it is very interesting to notice that the enzyme cells must be very rich in pentosans, since the removal of

this relatively small percentage of the endosperm brings the total percentage of pentosans down from 2.557 to 1.552.

It is also interesting to see how comparatively rich the endosperm and especially the starchy part of the endosperm is in methyl pentosans.   Applying the results in Table 3 to the results in Table 2, I find that the component parts of 100 gram, dry corn contain:

		Pentosan	Methyl Pentosan	Total
4.	Endosperm	1.45	.74	2.19
	Hulls	3.31	.41	3.72
	Germ	.63	.02	.65
	Total	5.39	,1.17	6.56

The disintegration of the corn on a factory scale is performed by soaking the corn with lukewarm water to which a small amount of sulphurous acid has been added until it is sufficiently softened for the milling process; then it is separated from the water and cracked in steel mills.   The germ can now be separated by mechanical means; it is dried and ground into germ meal containing about 55% oil, most of which is removed by pressing, leaving as a residue the corn oil cake still containing about 10% oil.   On a manufacturing scale it is naturally impossible to free the germ from particles of endosperm and especially hulls; furthermore it must be remembered that a great part of the organic phosphates and other extractive matter largely present in the germ has been removed during the steeping process, consequently I find a higher amount of pentosans present in factory samples than in laboratory-prepared samples.

Average analysis showed the following results:

		Pentosan	Methyl Pentosan	Total	100 parts Pentosan consist of	
					Pentosan	Methyl Pentosan
5.	Germ meal	11.43	.570	12.000	95.25	4.75
	Oil cake	23.00	.852	23.852	96.43	3.57

After separation of the germ the rest of the corn is ground in buhr mills.   The ground material is run over silk sieves which

70 SUGAR

25% SOLUTION IN ¼" CELL, LOVIBOND'S COLORIMETER
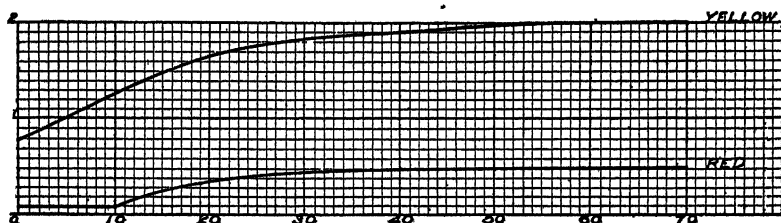
ORDINATES = LOVIBOND TINT-UNITS

ABSCISSAS = DAYS

separate the hulls from the liquid containing starch and gluten. This liquid runs over tables where most of the starch, called "green starch," settles while the gluten runs away with the tailings.

A part of this gluten which still contains 30 to 40% starch on dry basis is concentrated, filter-pressed and dried. This product is known as gluten meal.

The other part of the gluten liquor is mixed with the hulls, filter-pressed and dried together with the concentrated corn soluble, extracted during the steeping process. This product is known as gluten feed.

The following table gives the average analyses of these various products:

6.	Pentosan	Methyl Pentosan	100 parts total Pentosan consist of		
			Total	Pentosan	Methyl Pentosan
Gluten Meal	4.06	.496	4.556	89.11	10.89
Hulls	39.96	2.790	42.75	93.47	6.53
Corn Soluble	1.74	.462	2.202	79.02	20.98
Gluten Feed	18.58	1.21	19.79	93.89	6.11
Green Starch	.98	1.40	2.38	41.28	58.82

The corn soluble gives by the distillation furfural corresponding

CORN SYRUP (UNDILUTED)

σ CELL, LOVIBOND'S COLORIMETER
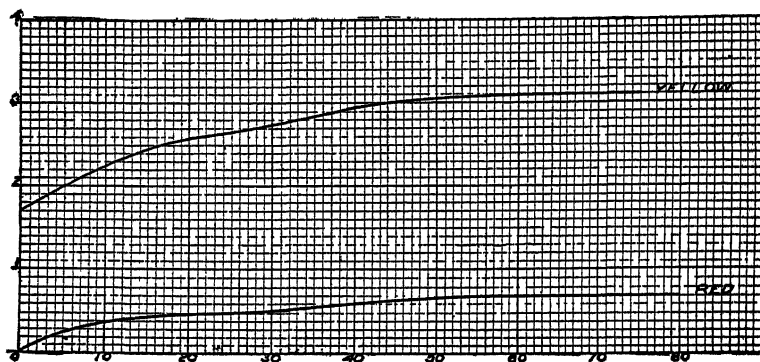
(ORDINATES = LOVIBOND TINT UNITS
(ABSCISSAS = DAYS)

to 2.202% pentosans, showing that the corn either contained pentoses which are extracted or that hydrolysis of pentosans has taken place in the steeping process. Before the green starch is used for food purposes it is washed first with weak solution of caustic soda and then several times with water; after each washing the starch is passed over silk sieves.

Average analysis of food starches:

7.

Pentosan	Methyl Pentosan	Total	100 parts total Pentosan consist of	
			Pentosan	Methyl Pentosan
.48	1.21	1.69	28.4	71.6

It will be seen from these results that even a very careful washing and sifting does not remove pentosans from the starch.

REFINERY PRODUCTS

These are the acid hydrolyzed products of corn starch either in syrup form—as corn syrup—or in form of crystallized glucose with more or less moisture content.

As we have seen, it is practically impossible to prepare corn starch free from pentosans, consequently we may expect to find

small amounts of pentosan hydrolyzation products in the various refinery products, and, as an ultimate product of the hydrolyzation, furfural.

Table 8 shows the percentage of pentosans present in starch used for the hydrolysis, and the amount of pentosan hydrolyzation products in the finished corn syrup and corn sugars which yield furfural by Tollens method. All results are given as pentosan and methyl pentosan, an absolutely dry basis.

8.	Pentosan	Methyl Pentosan	100 parts total Pentosan consist of		
			Total	Pentosan	Methyl Pentosan
Starch used for Corn Syrup	.623	1.26	1.883	33.09	66.91
Corn Syrup (42% Glucose on dry basis)	.776	.897	1.673	46.38	53.62
Anhydrous Sugar (97% Glucose on dry basis)	.722	1.18	1.902	37.96	62.04
Bread sugar (94½% Glucose on dry basis)	.656	.980	1.636	40.10	59.90
Hydrol (is the mother liquor from the bread sugar)	.860	1.79	2.650	32.45	67.55
Starch used for (80 and 70 sugars)	.649	1.24	1.889	34.36	65.64
80 Sugar (92% Glucose dry basis)	.68	1.06	1.740	39.08	60.92
70 Sugar (86½% Glucose dry basis)	.72	1.15	1.870	38.50	61.50

Every manufacturer of products of starch hydrolysis has noticed the more or less rapid colorization of syrup and sugars when these are stored for some time. The 3 sets of curves accompanying this paper show the rate of colorization in corn syrup, 80 and 70 sugar.

The ordinates indicate the units of the composing red and yellow colors according to Lovebond's standard and the abscissas indicate the number of days of storing under ordinary warehouse conditions.

The corn syrup was examined undiluted in a 6″ cell while the sugars were dissolved to a 25% solution and examined in a ½″ cell.

It will be seen that the curves after a certain number of days run parallel with the abscissas, showing that the color increase ceased.

It is undoubtedly a slow oxidation that has taken place here; addition of reducing agents to corn syrup and sugars, as for instance

sulphurous acid in the form of bisulphites, will check the color increase. As furfural may be considered as an ultimate product formed by the acid hydrolyzation of pentosans there is a possibility of its presence in hydrolyzation products of corn starch, and as furfural rapidly changes from a colorless solution when freshly prepared into a dark brown solution, when exposed to the air, we may draw the conclusion that the slow color increase of refinery products is due chiefly to the presence of traces of furfural. To comply with the pure food law, American manufacturers have abandoned the use of sulphites for preserving the color of corn syrup and sugars, but manufacturers in other countries use it as a general rule.

That sulphites check the colorization of furfural in corn syrup was shown by the following experiment:

To samples of corn syrup, which after storing showed a very slight but constant color, were added small percentages of furfural and to other samples the same amount and equivalent amounts of sodium bisulphite according to the reaction.

$$C^4H^3OCHO + NaHSO^3 = C^4H^3OCH (OH) SO^3Na.$$
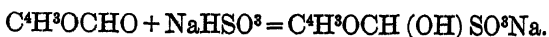
While the first series of samples showed a gradual increase of color the other series remained unchanged, retaining the same color as the original sample.

There is still another possibility for color increase which I shall mention here. The refinery starch will always contain traces of protein—about .05% nitrogen; while we are able to trace nearly all the pentosans in the starch down to the various refinery products, only very small amounts of nitrogeneous matter can be found here—corn syrup, for instance, containing only from .005 to .01%. But when the protein molecule is broken up during the conversion, traces of oxybenzoles or derivates of oxybenzoles may be formed, and it is a well-known fact that furfural, in connection with oxybenzoles, forms products of very pronounced colors.

RESEARCH ON LINTNER'S POLARIMETRIC METHOD FOR THE DETERMINATION OF STARCH

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Coytesville, N. J.

Desiring a quicker and more accurate method than the diastase method for the determination of starch in corn and corn products, the authors decided to investigate Lintner's polarimetric method, which appeared to be promising, to see if it were applicable to corn products. It was therefore necessary to try it out under various conditions to establish its reliability.

The greatest source of error is the hydrolyzation or partial hydrolyzation of the starch by the concentrated acid. Therefore the authors made a study on a pure corn starch under various conditions to determine those under which hydrolyzation is minimum or constant.

Several tests were made with weights of starch varying from 0.1 gram to 15 grams but the readings were not exact multiples of the various weights, therefore 5 grams were arbitrarily chosen. Readings were made in a Schmidt and Hänsch half-shadow polariscope with triple field of vision, in a 200 mm. tube and expressed in degrees Ventzke.

When water is added to starch, there is an elevation of the temperature and when concentrated hydrochloric acid is added to the mixture, the temperature rises still more, due to the heat of dilution of the acid and an exothermic reaction between the starch and the acid. Therefore it was found necessary to cool down the starch and water mixture and to keep the hydrochloric acid in a freezing mixture. The following test made roughly will show the heat effects:

Fifteen grams pure starch, 50 cc. water and 100 cc. concentrated HCl were cooled down in separate beakers. The water was added to the starch, to which the hydrochloric acid was then added.

Temperature of starch $=14.1°$ C.

Mixture $=16.5°$ C.

Temperature of water $=14.0°$ C.

Temperature of HCl $=10.0°$ C.

$$\left.\begin{array}{l}\text{Mixture starch}\\\text{Water and acid}\end{array}\right\} =29.4° \text{ C.}$$

1. *Effect* of *Varying the Temperature of Steeping with Concentrated HCl.*

Weight of starch taken, 5 gms.; time of steeping, 30 minutes; time of standing after steeping to time of reading, 45 minutes.

All temperatures were brought to 20° C. immediately after steeping.

Temperature HCl	Temperature Starch water HCl	Temperature during the 30 min steep	Reading
3.5° C.	14.2° C.	5.° C.	26.7° C.
	13.2° C.	5.° C.	26.6° C.
	12.2° C.	10.° C.	26.3° C.
2.0° C.	12.5° C.	10.° C.	26.3° C.
2.6° C.	8.0° C.	10.° C.	26.4° C.
1.0° C.	12.2° C.	15.° C.	26.3° C.
2.0° C.	12.5° C.	15.° C.	26.3° C.
0.° C.	12.8° C.	15.° C.	26.3° C.
3.2° C.	18.8° C.	20.° C.	26.0° C.
0.6° C.	20.0° C.	20.° C.	26.0° C.
2.7° C.	18.8° C.	20.° C.	26.0° C.
3.5° C.	18.4° C.	25.° C.	25.6° C.
4.0° C.	19.0° C.	25.° C.	25.6° C.
3.0° C.	20.5° C.	25.° C.	25.6° C.

It is evident that the hydrolysis is less at the lower temperatures, but, due to the exothermic reactions, it would not be practicable to work at those temperatures. Twenty degrees Centigrade has been found to be the most convenient temperature.

2. *Time of Steep Variable.*

Weight starch, 5 gms.; temperature of steep, 20.° C.

Time of standing after steeping to time of reading was made 45 minutes.

Temperature HCl	Temperature Mixture	Time of steeping with conc. HCl	Reading
6.0° C.	17.3° C.	5 min.	25.8° C.
3.1° C.	16.4° C.	10 min.	26.3° C.
5.0° C.	14.5° C.	15 min.	26.3° C.
3.5° C.	16.3° C.	20 min.	25.9° C.
5.0° C.	14.6° C.	25 min.	25.95° C.
2.9° C.	24.5° C.	35 min.	25.7° C.
6.4° C.	24.6° C.	40 min.	25.6° C.

We found that steeping for five minutes is not sufficient for all the starch to go into solution. After reaching the maximum, the readings decrease with increase in time of steeping.

3. *Time of Standing after Adding Phosphotungstic Acid until Reading is Taken, Variable.*

Weight starch, 5 gms.; temperature of steep, 20.° C.; time of steep, 30 minutes.

Time of Standing	Reading	Time of Standing	Reading	Time of Standing	Reading
½ hour	26.2	3 hrs. 11 min.	25.6	5 hrs. 4 min.	25.4
½ hour	26.2	3 hrs. 15 min.	25.5	5 hrs. 7 min.	25.3
1 hour	25.8	3 hrs. 13 min.	25.6	5 hrs. 7 min.	25.3
1 hour	25.8	3 hrs. 26 min.	25.4	5 hrs. 6 min.	25.2

The hydrolyzation of the starch increases as the time of standing continues. However, it seems to be constant for a given time of standing. The change is greater during the first three hours than during the subsequent two.

4. The following set was run with the time of standing, until the reading was taken, constant at 45 minutes. After steeping, the phosphotungstic acid was added and the solution made up to 200 cc. with hydrochloric acid of 1.125 specific gravity and allowed to stand 30 minutes ·in a water bath kept at 20.° C. Then it was filtered, and exactly 15 minutes later the reading was taken.

Weight starch, 5 gms.; temperature of steep, 20.° C.; time of steep, 30 minutes; time of standing to reading, 45 minutes.

Temperature HCl	Temperature Mixture	Reading
2.4° C.	20.8° C.	26.0° C.
2.4° C.	22.6° C.	26.0° C.
2.7° C.	21.7° C.	26.0° C.
1.5° C.	20.2° C.	26.0° C.
0.5° C.		26.05° C.

5. In all the preceding cases, 10 cc. of a 4% water solution of phosphotungstic acid were used. In the following set, the amount was varied, other conditions being constant. The required amount of a 20% solution was made up with water to 10 cc. and then added to the starch solution.

Weight starch, 5 gms; temperature of steep, 20° C.; time of steep, 30 minutes; time of standing from steep to reading, 45 minutes.

Amount of Phosphotungstic Acid	Reading
nil	26.3° C.
5 cc. of 4% solution	26.1° C.
5 cc. of 4% solution	26.1° C.
3 cc. of 20% solution equivalent to 15 cc. 4%	25.6° C.
4 cc. of 20% solution equivalent to 20 cc. 4%	25.3° C.
5 cc. of 20% solution equivalent to 25 cc. 4%	25.1° C.
6 cc. of 20% solution equivalent to 30 cc. 4%	24.8° C.
7 cc. of 20% solution equivalent to 35 cc. 4%	24.9° C.
8 cc. of 20% solution equivalent to 40 cc. 4%	24.6° C.
9 cc. of 20% solution equivalent to 45 cc. 4%	24.4° C.
10 cc. of 20% solution equivalent to 50 cc. 4%	24.4° C.

The white hydrated tungstic acid was precipitated in each flask containing the equivalent of 15 cc. or more of a 4% phosphotungstic acid solution, increasing in volume with the amount of phosphotungstic acid added. Some starch was also thrown down, since the reading diminishes with increase in phosphotungstic acid.

Many other determinations were made on the same pure starch with all conditions constant.

Weight starch, 5 gms.; time of steep, 30 minutes; temperature, 20.° C.; time of standing from steep to reading, 45 minutes; amount of phosphotungstic acid, 10 cc. of 4% solution.

In all, the readings were 26.0° V. From this value the specific rotatory power of dry corn starch was computed to be 199.413°, the moisture in the starch being 10.038%.

Observing the conditions of time and temperature, the method will read as follows:

Five gms. of starch, or a weight of the finely ground substance equivalent to 5 gms. starch, are mixed with 20 cc. of water in a mortar, cooled down in ice water. To this is added 40 cc. concentrated HCl previously cooled down in a freezing mixture, and then the solution is kept at 20.° C. for $\frac{1}{2}$ hour. The contents of the mortar are then transferred to a 200 cc. flask, 10 cc. of a 4% phosphotungstic acid solution added, and made up to the mark at 20.° C. with HCl of 1.125 specific gravity. The flask is then kept for $\frac{1}{2}$ hour in a water bath at 20.° C., filtered and, exactly 15 minutes after filtering, the reading is taken at 20.° C.

The method was now applied to the determination of the starch in the corn kernels. Many determinations were made taking 7 grams of the ground corn in work and the readings checked well. A correction for the water solubles was made by taking an aliquot part of the water solution representing 7 grams original sample, and substracting this from the readings obtained for the corn.

The diastase method was used for comparison.

Starch in the corn on dry basis, Lintner's method — 68.62%.

Starch in the corn on dry basis, diastase method — 68.54%.

A sample of an intermediate product, obtained in the manufacture of corn products from the disintegrated maize kernels consisting chiefly of hulls with some adhering starch from the endosperm, was tried and compared with the diastase method, the results checking well.

Lintner's method — 17.2% starch on dry basis.

Diastase method — 17.3% starch on dry basis.

The authors next desired to test the method with a product high in protein content and so took samples of gluten meal, which is a product very rich in gluten (protein from 40 to 50%). It was found that the polarimetric readings increased with the amount

of phosphotungstic acid which precipitates the protein. The maximum reading was obtained when 10 cc. of a 20% solution, equivalent to 50 cc. of a 4% solution, were used. Then, as more phosphotungstic acid was added, the readings gradually became lower, due to the precipitation of some starch, as we have shown in Table No. 5.

The percentage of starch on dry basis corresponding to the maximum reading was 44.7%.

Sachsse's method gave 45.2%.

CONCLUSIONS

1. Results are concordant when the same conditions are observed.

2. The method checks fairly well with the diastase and Sachsse methods.

3. It is rapid, taking only 1 hour and 15 minutes.

4. Results are evidently too low when an excess of protein is present.

5. The worker is not troubled by HCl fumes when the temperature is kept at 20.° C.

BAMBOO CELLULOSE

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India

1. In this paper is given a condensed account of the results of an enquiry into the cellulose yielding possibilities of Indian bamboos.   Any one desirous of following up the investigation in its full details is recommended to obtain Part III of Vol. III of "The Indian Forest Records" which will shortly be published by the Superintendent, Government Printing, Calcutta, and which will contain the official report of the enquiry.

2. A survey of the research work already accomplished by Sindall, Richmond and others, and of detailed reports of a number of large-scale factory tests made in India and England resulted in the preparation of a "present position" statement as follows:

a.   A general agreement as to the suitability of bamboo cellulose for the manufacture of paper, and especially of printing and litho grades, provided its isolation has been successfully accomplished.

b.   A general agreement that reduction by soda is the only practical method applicable and that the bi-sulphite process is unsuitable.

c.   A general agreement that the nodes are irreducible within practical cost limits and that they must be cut out and rejected.

d.   In regard to internodes a great divergence of opinion and statement as to the practical results obtained, soda consumption varying from 16 to 40%, bleaching powder from 9 to 40% and cellulose yield from 33 to 50%.   Some experimentalists claim even and regular digestion, while others assert that the results are irregular and frequently spoilt by the presence of hard and imperfectly digested matter.

It was resolved that the present investigation, while taking full advantage of all that had previously been done and reported, should concern itself specially, 1st, with the points upon which

opinion and results varied, in an attempt either to reconcile the divergencies or to eliminate their causes, and 2nd, in an endeavour to utilise the nodes, it being recognised that their rejection constitutes a serious drawback to the successful exploitation of bamboo, not merely in the waste of from 7 to 15% of raw material but also in the troublesome and costly nature of the cutting-out process owing to the destructive effect of the siliceous cuticle on steel cutting edges.

3.   Previous workers in this field have laboured under serious disadvantages on account of the little that was known of bamboo economics.   Hitherto regarded as a more or less waste and worthless jungle product, scarcely any attention has been given to the collection of information dealing with its commercial exploitation on a large scale.   The bearing of this state of ignorance upon the causes of the divergent opinions and results referred to above is obvious.   It might be the case that some of these were due to peculiarities of species which were of no commercial importance. With species numbering some hundreds growing over a wide range and variety of latitude, elevation, climate and soil, it would not be surprising if a considerable difference in results should occur.   It did therefore appear that a necessary preliminary to this investigation must be a systematic enquiry into the exploitation economics of bamboo.

4.   Such an enquiry was duly instituted and carried out by Mr. R. S. Pearson of the Indian Forest Service, official Forest Economist to the Government of India.   His report came to the somewhat surprising, but perfectly well founded, conclusion that out of the many species available in India and Burma only five, *viz.*, Bambusa Tulda, B. arundinacea, B. polymorpha, Cephalostachyum pergacile and Melocanna bambusoides, exist in commercial quantities and under economically exploitable conditions. Though few in number these species are each so dominant in their own areas that they probably represent 80% of the whole growing stand of bamboo in the country, and it is somewhat remarkable that they are the sorts that have hitherto proved easiest to treat and that several of those which have been excluded do present difficulties, peculiar to themselves, sufficient to account for some of the contradictory results which have been recorded.

But while thus limiting and simplifying the problems before the experimenter, Mr. Pearson's report did introduce a new difficulty which we had not anticipated. We have hitherto paid considerable attention to bamboo as a plant whose resistance to reduction increased with age and much time and effort has been expended on the establishment of degrees of treatment suitable for various ages. Now we learn that all this has been wasted and useless labour for the simple reason that in large-scale forest exploitation, differentiation as to age is impossible, that there are no indications whatever enabling one to distinguish between 2, 3, 4 or 5 year old stems and that even in the case of yearling culms their slight difference of appearance disappears after a few weeks' drying. In short, we must deal with bamboo of all ages, mixed and as a whole or not at all, and all we can hope to do in the way of selection is to keep species separate.

5. A short experience of bamboo digestion enables us to suggest the following as being among the more obvious reasons for its difficulties and for the irregularity and imperfection in the results:—

a. Its tendency to float, permitting a portion of the digester charge to be buoyed up out of contact with the liquor for a considerable time.

b. Its resistance to liquor penetration and the variation of this in accordance with the size of the chip, small chips digesting more quickly and more perfectly than large ones. Also the variation in this respect in accordance with age, a charge of mixed age being invariably irregularly digested.

An examination of its structural, physical and microscopic features yielded the following results:—

6. *Specific Gravity.* A bamboo culm is light and bouyant solely because it is hollow. Its component wood is really as heavy as many of our commercial hardwoods. Its actual specific gravity varies somewhat with species, that of the lightest of the five species we are concerned with being .8410 for internodes and .8091 for nodes, while the heaviest is .9555 internodes, and .9170 nodes. These results are on two year old samples but the figures do not appreciably vary with age after maturity (one year) has been reached. It is important to note that nodes are actually

lighter than internodes, therefore their greater resistance to digestion is not due to greater density. Bamboo is therefore of about twice the specific gravity of the common pulp woods, spruce and fir, a fact which, when realised in all its bearings, throws considerable doubt to whether we have been right in treating it on similar lines as to wood so far as its preliminary preparation for digestion is concerned.

7. *Capillary Air.* A marked microscopic feature of bamboo is the sap canals or vessels of comparatively large size and visible with a low power lens. They appear in groups of four arranged in the form of rhomboid squares. The groups are about 1 mm. distant from each other, and in the groups the tubes are about 0.5 m.m. apart. Their diameter is 0.1 m.m., mostly circular in shape though occasionally one of oval contour is found. In a bamboo of 3 inches' diameter with walls half an inch thick there are about 8000 of them. They run in continuous and uninterrupted parallel series throughout the whole length of the culm and are not broken at the nodes but merely slightly displaced from the true parallel and vertical direction. They do not collapse in drying but retain their full size and shape and consequently their air-carrying capacity. Dry bamboo is therefore largely impregnated with air in a state of capillarity, a condition which makes it somewhat difficult to expel and which fully accounts for the tendency to float which is one of the chief difficulties in its digestion. When a mass of bamboo chips is boiled in an open vessel and prevented from floating by being held under the water surface, the expelled air forms a dense dome of froth over the water. Spruce chips similarly dealt with throw up a few air bubbles only. When not prevented from floating, bamboo floats considerably longer than spruce in spite of its greater specific gravity. The greater lightness of spruce permits a much larger proportion of its mass to be buoyed up out of contact with the water, but the whole of the buoyed portion sinks under the surface much sooner than the smaller bouyed portion of bamboo. The capillary air in the latter resists soakage longer and it cannot wholly sink until this has been expelled and its place taken by water. In an experiment made with equal quantities of bamboo and spruce chips, thrown into open vessels containing equal volumes of NaOH

liquor, and boiled, the spruce took one hour to wholly sink while the bamboo required two and a half hours. When forcibly sunk and held under the surface by a perforated plate and then boiled, it continues to throw up air bubbles for two hours. It is not difficult to appreciate the light which this throws upon some of the digestion failures of the past and it supplies another reason for doubt as to whether we have been justified in basing our treatment of bamboo upon our experience with wood.

8. *Structural Resistance.* Here again we find conditions differing totally from those of spruce which is almost equally resistant in all directions to mechanical disintegration, but being a soft wood of low specific gravity it has little mass resistance to the soakage and penetration of liquor. Bamboo is a hard and heavy material but is strongly resistant to mechanical force in the transverse direction only. To a splitting or crushing force acting longitudinally, it has scarcely any resistance whatever and it is possible by careful dissection to isolate individual filaments or fibre bundles and to follow them up along the nodes and through the internodes for the whole length of the culm. It is this facility of separation of its fibrous structure and absence of interlacing with adjoining filaments, together with the large interior surface of the sap canals exposed to chemical action (provided the air is expelled), which permits us to remove it from the category of impervious hard woods in which its high specific gravity and transverse hardness would otherwise place it. But, in chips, with its transverse hardness not destroyed and its capillary air not expelled, it presents a mass resistance to the penetration of solvents immensely greater than spruce.

9. A physical and microscopical examination therefore leads to the following conclusions, *viz.*, that the digestion difficulties are to a considerable extent due to:—

a. A mass or structural resistance to penetration of liquor varying with the size of the individual chip, therefore the smaller the particles and the more regular their size the better will be the results.

b. The resistance of the capillary air. If this could be expelled prior to digestion so that the liquor would be free to at once attack the interior of the sap vessels, the benefit would no doubt be great.

It is also clear that the greater difficulties presented by both the nodes and the older internodes is not due to greater density. An explanation of it must be sought in their chemical composition.

10.   The scheme of analysis adopted is based wholly on the varying solubilities of the component substances as follows:

Group I.   Matter soluble in water at 100°C., chiefly starch and its transformation products, with colouring matter and soluble salts.

Group II.   Matter soluble in 1% NaOH at 100°C., chiefly pectose with small quantities of fat and wax. (When isolated by hot ether-alcohol treatment the latter varies in amount with species from 0.75 to 1.70%. Resides chiefly in the cuticle.)

Group III.   Lignin, soluble only in strong NaOH at temperatures above 130 C.

Group IV.   Cellulose, the insoluble residue from the sodium hydroxide-chlorine-sodium sulphite treatment of Messrs. Cross and Bevan.

Ash is not included in the percentage proportions because each of the above groups carries out with it its own complement of silica or salts or both. To include it would therefore have the effect of reckoning it twice. *Hydroscopic moisture* is also excluded, all the determinations being made on the absolutely dry substance. The following on dry seasoned B. polymorpha is typical of all the species mentioned except Melocanna B. which has more lignin and less pectose. The whole culm sample taken contained both nodal and internodal substances in their strict proportions as they exist in a whole culm.

| | WHOLE CULM | | | | | Inter-nodes |
	Young culm ¾ grown	One year old	Two years old	Three years old	Nodes only 2 years	nodes only 2 years
G. I. Starch, etc.	13.10	11.60	8.95	6.90	9.83	8.70
G. II. Pectose, etc.	25.23	19.02	20.60	22.52	26.44	20.19
G. III. Lignin	5.62	15.66	15.74	15.96	17.60	15.29
Cellulose	56.05	53.72	54.71	54.62	46.13	55.82
	100.00	100.00	100.00	100.00	100.00	100.00
Ash	2.61	4.73	3.97	2.18	4.50	3.87

The analyses may be interpreted thus:—lignification begins with the sprouting of the branches which occurs when the culm is three-fourths grown and is complete at one year old, little or no change in this respect happening afterwards. At the half-grown stage the plant is wholly pecto-cellulose in character. With the rapid increase in lignin at maturity there is a corresponding reduction in pectose, but with advancing age a gradual increase in the latter at the expense of the starch group.

Nodes compared with internodes show a large increase in pectose and rather more lignin.

11. The plant is distinctly of a pecto-ligno-cellulose character, having both pectose and lignin in considerable quantity and thereby differing seriously from any other material in common use. I have determined the effects of the three groups of solubles upon soda consumption to be approximately as follows:

Group I   combines with 0.22 for each 1% in the analysis.
Group II   combines with 0.32 for each 1% in the analysis.
Group III combines with 0.66 for each 1% in the analysis.

These figures are for complete but *bare* digestion only, under suitable conditions of time and temperature, and do not take into account any excess of NaOH which it may be advisable to use to obtain a bleaching effect. If we now calculate the quantity of soda required for one and three year old in accordance with the above figures we get:

	1 year old at NaOH		3 year old at NaOH
Gr. I	11.60 c 0.22 = 2.55		6.90 c 0.22 = 1.52
Gr. II	19.02 c 0.32 = 6.09		22.52 c 0.32 = 7.21
Gr. III	15.66 c 0.66 = 10.34		15.96 c 0.66 = 10.53
Add ½ per cent excess	.50		.50
Per cent required on dry raw material	19.48		19.76
Per cent on air dry	17.54		17.79

Similarly on the node and internode analysis we get a theoretical consumption for the latter of 17.07% and for the former 20.47%. Three year old ought therefore to digest satisfactorily with the same consumption of NaOH as one year old, and nodes with 3½%

more than internodes. What actually occurs is this: in one year old the internodal chips are fairly well digested but the nodal chips are not; in three year old, internodal chips are badly digested and nodal ones scarcely softened. Internode chips digested by themselves with 17% yield good results but node chips by themselves will not digest with even 30%. But, if instead of dealing with the material in chips we reduce it by *crushing* to an extremely fine state of sub-division of filaments, the whole difficulty disappears at once. A whole stem, nodes included, when suitably crushed will digest satisfactorily with the theoretical $17\frac{1}{2}$ or 18% of NaOH and it makes no difference whether it is one or three year old, and in the product there is absolutely no indication whatever of the nodes. All good pulp and no chips.

12. We have already seen (paragraph 9) that the greater resistance of old bamboo and especially of nodes is not due to greater density. Neither can we attribute it to capillary air which can only delay and not prevent digestion and, in any case, there is no difference in this respect noticeable between old and young stems or between nodes and internodes. The only variation remaining which can have any effect is in the *pectose* contents which are $5\frac{1}{4}$% greater in three year old than in one, and 6% more in nodes than internodes. But, as shown by the soda estimates (in paragraph 11), these increases do not call for any greater consumption in the case of three year old and for only $3\frac{1}{2}$% more for nodes. I therefore hazard the hypothesis that the secret of the whole trouble lies in the greater physical resistance to liquor penetration created by the larger and thicker masses or films of pectose matter in which the filaments of the nodes and older internodes are buried. When we consider that under the normal conditions of digestion, *viz.*, high temperature and strong NaOH, pectose *gelatinises*, it does not appear impossible to imagine a colloidal resistance set up similar to that which occurs on the surface of a lump of resin when thrown into boiling NaOH, or upon a cake of gelatine when put into hot water. Such a colloidal result would exercise a protective effect upon the lignin, especially in the interior of a chip where the colloidal films or masses and the matter which they enclosed would be more or less imprisoned and hindered from floating away freely in the liquor. But *crushing*

counteracts this imprisonment, and by reducing the pectose masses and films from large to small and thick to thin and destroying their mere physical cohesion, the colloidal resistance is reduced in a similar manner to that of the lump of resin above referred to when it is crushed to powder and in that condition added to the boiling NaOH. The immensely greater surface area presented to the action of the liquor by the fine particles prevents a colloidal effect being established. Any how, whatever may be the true reason, the fact remains that crushing solves the difficulty, not only as regards mixed ages, but also that of the nodes, and the whole bamboo can now be digested with no more (or very slightly more) than its theoretical quantity of soda and at a lower temperature and in a shorter time than in the case of chips with nodes excluded.

13. Crushing, when thoroughly done, reduces the whole bamboo to soft fibrous masses something like hanks of coarse tow and with its original brittleness largely destroyed. The distinctive appearance of the nodes is lost, it being difficult to tell, in the crushed mass, which is node or internode. This result is largely aided by the structural features mentioned in paragraphs 7 and 8. The crushing fracture runs along the groups of capillary tubes which form weak places in the wall and which split open. The capillary air trouble is thus got rid of and the interior of the tubes opened up to immediate attack by the liquor. This means that the floating trouble is got rid of and the period of digestion reduced. So completely is the air resistance destroyed that the sp. gr. of crushed bamboo is greater than that of chips, and the lightest species float for only ten minutes while the heavier sink at once. Chips will float for $2\frac{1}{2}$ hours (see paragraph 7).

14. I therefore come to the conclusion that the chief difficulties hitherto found in the digestion of bamboos are of a physical rather than a chemical nature and they must be, and can be, conquered by physical means. To recapitulate, they are, or have been:—

  a. The impossibility of digesting nodes.

  b. The tendency to float.

  c. Mass resistance to liquor penetration considerably greater than that of spruce and varying with the size of the chip.

   d.   Capillary air resistance to liquor penetration.
   e.   Resistance increasing with age.
   f.   A possible colloidal resistance of gelatinised pectose.
Each and all of which are wholly got rid of or very much reduced in difficulty by crushing.

   15.   One of the difficulties remaining is connected with the starch content of the plant and its effect upon yield of cellulose and also on the bleaching results.   In its annual reproduction of new culms, bamboo is unique, inasmuch as the whole of these reach their full height within a period of from two to four months. This enormous and rapid effort may result in new growth equalling, in actual dry weight, one-fifth to one-fourth of that of the whole clump, and the normal activity of its root and leaf systems would be wholly inadequate to support it were these not aided by its power of storing up large reserves of plant food in anticipation, chiefly in its roots but also to a very considerable extent in its culms.   From these reserves the young shoots draw the major portion of the material required for building up their tissues. These reserves consist of starch in its solid and granular form. During the process of its transformation into woody tissue it breaks down, or metamorphoses, into several groups of secondary products, all of which are soluble in cold water and therefore capable of being assimilated by the plant.   Both as starch and as secondary starchy matter, it at all times and seasons forms a considerable constituent of bamboo and one not met with to any appreciable amount in other raw materials.   But its special interest to us is its liability to large variation at different seasons of the year.   As the young culms make their appearance at about three to five weeks after the commencement of the southwest monsoon, we find the largest reserve stores existing then, the first few weeks of the monsoon season, as also the period of showery weather preceding it, having been utilised to collect them; and we also find, as we should expect, that they are at their lowest at six to eight weeks after the monsoon has ceased and when the young stems are fully grown.   But should a period of showery weather intervene during seasons which are usually dry, or if the district is visited by the short northeast monsoon, the habit of the plant asserts itself and storage takes place, resulting in the upsetting of

the normal relative percentage of its constituents. I have found, for instance, in a bamboo cut during the height of the dry season a total water extract of 9 per cent on the dry substance, a period of unusual and unseasonable showery weather, lasting for three weeks, then intervened. A culm cut from the same clump then yielded 23% of water solubles with, of course, a relative reduction of the cellulose which was only 37%. But it is important to note that this same culm, preserved in a dry atmosphere for five weeks, yielded then only 15 per cent of water extract, which three months later fell to 11 per cent with corresponding rises in the relative percentage of cellulose. This can only mean that the starch is, in its secondary forms, capable of being oxidised by air and dispersed in the atmosphere, and that such oxidation is an integral part of the process of seasoning, and it forces us to the conclusion that the maximum relative yield of cellulose can only be obtained from bamboo which is not merely dry but is also *seasoned.* We have in this a highly probable reason for the few instances of 33% to 35% yields reported. In my own experiments, numbering some hundreds, results obtained from *seasoned* bamboo of all five species run to a remarkably close and regular average of 45% of unbleached pulp.

16. The influence of the starch content upon bleaching is due to the result of the combination between it and NaOH which occurs under the digestion conditions of strong liquor and high temperature. A detailed analysis of the water solubles of a stem cut at a period when the food stores were being used gave the following results:

	Per cent
Starch, solid	2.70
Starch in secondary forms	8.33
Colouring matter and soluble salts	2.54
	13.57

The result of the combination of solid starch with NaOH is colourless and soluble and so does no harm, but that with the secondary starch matter is an insoluble dark brown precipitate which the pulp filters out and which is unbleachable (within

economic limits) and seriously affects the bleaching of the pulp. The quantity of NaOH which may thus be abstracted from the liquor is about 0.22 for each 1% of solubles present, so that with a sample containing 9%, about 2% of NaOH, on weight of raw material, will be thus used up. Since they are soluble in hot water, obviously the right course is to make a preliminary boiling in water the first step in digestion. After thus exhausting them the digestion can then proceed with a reduced quantity of NaOH. Pulp thus treated will bleach with 4 to 6% less bleaching powder.

17. Notwithstanding the improved bleaching conditions thus brought about, the bleaching qualities of the pulp, when prepared with the *minimum* quantity of NaOH required for digestion, still leave much to be desired. A typical result, on crushed and starch-exhausted *Bambusa polymorpha,* is as follows:

NaOH, on air dry weight of raw material	16%
Initial temperature for 1 hour	177 deg. C.
Subsequent temperature for 4 hours	162 deg. C.
Duration of digestion	5 hours
Unbleached yield, air dry	50%
Bleaching powder used on A.D. weight of unbleached pulp	36%
Bleached yield, air dry	44.5%

The digestion was perfect as far as freedom from chips and imperfectly digested material goes but the pulp was of a very dark brown colour and required 36% of bleaching powder to bring it up to a brilliant white. The wide difference between the unbleached and bleached yields will be noted and is clearly due, in large measure, to precipitation of colouring matter which can only come from the gelatinised pectose which, as already remarked, is dark brown in colour, and is almost unbleachable. A problem familiar to all paper-makers who pulp grasses is the extent to which it is profitable to gain in colour at the expense of yield by using an excess of NaOH. Such excess does intensify hydrolysis of fibre but with the compensation of improved colour, presumably either by holding the coloured products more perfectly in solution, thus permitting them to be more thoroughly washed out of the

pulp, or by changing them to compounds of lighter colour. A series of experiments to determine the profitable limit of excess for bamboo resulted in it being fixed at 4%. The average result with exactly similar conditions of material, temperature and duration of digestion as quoted above being:

NaOH	19½%
Unbleached yield	45.5%
Bleaching powder used	25%
Bleached yield	43%

That is to say, an excess consumption of 3½% of NaOH resulted in a loss of 1½% in the final result and saving of 11% of bleach. This was satisfactory but not wholly so and we therefore endeavoured to find a better solution of the difficulty in the sulphate modification of the soda process. This process seemed to be very clearly indicated when we found that a one per cent solution of sodium sulphide, applied in simple cold steeping to the unbleached pulp produced by NaOH, dissolved out of it a large quantity of dark brown colouring matter, leaving it several shades lighter in colour and much more bleachable.

18.   The liquor used contained sodium sulphide and hydroxide in the proportion of 1:3. In the following average result the whole is reckoned in terms of NaOH. Material, temperature and duration of digestion as before.

NaOH	20½%
Unbleached yield	46%
Bleaching powder used	17%
Bleached yield	44%

The soda required is 1% more than with straight soda liquor as a compensatory allowance for the lower digestion efficiency of the Na_2S, but the bleaching effect of the latter, as also its influence in retarding hydrolysis of fibre, is most marked and undeniable, and our final conclusion is that the objections which have been made to bamboo as a paper-making material and the difficulties hitherto met with in its treatment, *viz.*, irregular yields,

floating, resistance to bleaching, mass, capillary air and colloidal resistance to liquor penetration causing irregular and imperfect digestion, the difficulty of dealing with mixed ages and the impossibility of economically treating the nodes, — can all bo met and solved and the whole problem reduced to one of extrcme simplicity by the adoption of a scheme of treatment embracing the following features:

    I.   Seasoned bamboo only to be used.
   II.   Raw material to be crushed.
  III.   Water solubles to be extracted previous to digestion.
   IV.   Digestion with sulphate liquor.

19.   It should be understood that the foregoing refers only to the five leading species of India and Burma and may not prove altogether applicable to bamboos of other species grown elsewhere.

A NEW TECHNICAL DETERMINATION OF BLEACHING QUALITY OF SULPHITE PULP

By Dr. Erich Richter

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In May, 1912,[1] I had been able to show that what is called the Hempel's nitric acid figure of pulp, that is, a treatment of sulphite or other pulp with a 13 per cent nitric acid for one hour in a boiling water bath, drawing air through and measuring the gases produced, can be easily converted in a method to determine the percentage non-cellulose in pulp, jute, or wood.

To get Hempel's nitric acid figure,[2] ordinary pulp, for instance, is somewhat broken up and submitted to a treatment with nitric acid as mentioned above. The gases are drawn through suitable absorption apparatus filled with water and at last with sulphuric acid. The nitric and nitrous acids which are formed can be titrated with standard solution of permanganate of potassium and one hundred normal caustic soda solution.

In order to get the percentage of non-cellulose or lignin, the same operation is done with pulp, which has been previously extracted with ether, alcohol and water. The percentage of lignin is then figured with a proper standard figure for jute or wood. For spruce wood I have found 1,076 grs. $N_2O_3 = 28\%$ lignin and for the nitric acid figure 0,8048 I made equal 40.

Investigation of both kinds on quite a number of different sulphite pulps, together with other tests, showed that the nitric acid figure gave values proportional to the bleach test, and as the latter is not very convenient, for instance, when it is necessary to test one, two, or more carloads of pulp on bleaching quality in a few hours, as it often happens in a pulp or paper mill, it has been tried to replace the same by the nitric acid figure. Being unable to find the right formula to convert this figure in per cent bleach powder for the pulp sample in an endeavor to reduce the time used for testing and to make the method as simple as possible,

[1] Wochenblatt fur Papierfabrikation p. 1631.
[2] Hempel v. Seidel, Diss Dresden

it occurred to me that a color test might do the work, provided it would give results within half per cent.

According to Klason,[1] the non-cellulose in pulp can be tested colorimetrically when ordinary pulp is treated with standard sulphuric acid. In Germany, a mixture of 4 parts of concentrated acid and 1 part of water is used. Others use stronger acids.

With sulphite pulps of different origin, tested on lignin, cellulose, bleaching quality, etc., series of experiments were made according to Klason, using one or another pulp as a standard sample. Unfortunately, in too many cases the results differed so much, not only in comparison with different percentage on non-cellulose, but also compared with the bleaching quality, that it was obvious that this method could not replace either the lignin test or the test for bleaching. It could be easily seen that sulphite with little non-cellulose, but soft-cooked, gave a much darker color with sulphuric acid than a strong-cooked pulp which sometimes contained 2% more lignin, that is, about equivalent to 7–8% more bleach powder. The reason for this is that a sulphuric acid not only attacks the non-cellulose, but also, especially in the case of soft pulp, it attacks too much the pure cellulose. After trying the method with sulphuric acid of different strengths and failing to get good results, another acid was used. Naturally, attention was drawn towards the diluted nitric acid.

Preliminary tests with nitric acid (about 13% HNO_3) showed sufficient agreement, and further investigations proved the success of this method, tests with it sometimes causing the revision of ordinary experiments on bleaching quality.

To make a test 5 grs. of air-dried pulp are broken up in thin pieces, put in a wide-necked bottle together with 100 cc. of standard nitric acid, well shaken, and kept for about one hour in a dark place. After that time it is again well shaken and the pulp filtered off, best by means of a little piece of pure absorbent cotton in the bottom of a dry funnel. From the liquid 25 cc. are taken and poured in a small bottle. With standard pulp of well known bleaching quality the same operation is performed at the same time, and both liquids are now compared in color. From a burette water is added to the darker one until the shade of both solutions

[1] Papierzeitung 35, 3781.

is the same. Suitable amounts of each acid solution are then put in Eggertz carbon tubes and compared. This is best done by looking down from the upper end, keeping a white paper below and using different amounts, once 5 cc., another time 10 cc. Should the colors not be uniform, as an additional check, a greater depth of the lighter liquid is used until the shades are the same. It is then easy to figure the bleaching capacity of the unknown sulphite.

	Total amount of acid a. water used
%Bleach powder	
Standard pulp....8,5%	25 cc.
Unknown Sulphite ...x	25 cc.×12 cc.

$$x = \frac{8,5.\ 37}{25} = 12,6$$

Should the first test be spoiled, another 25 cc. can be used without delay.

When breaking up the pulp, not much time is spent, as it need not be finely beaten up like in a regular bleaching test. A moisture test of the pulp should be made, at the same time, although it is not necessary to be very exact, as I have found that a few per cent difference in moisture does not influence the result to any noticeable extent, owing to the great excess of intric acid. When wet pulp has to be tested it must be dried somewhat and in order to facilitate the operations it is best broken up first. One thing more should be mentioned; a very strong cooked pulp sometimes would not color the acid after only one hour. In case a test cannot be delayed, the bottles are placed in a water bath of about 40° C. and frequently shaken. The temperature should not exceed 45°C. In about 15 minutes the acid colors almost instantaneously, and after cooling down a little the test is made as described above.

Performed in one way or the other, the method gave excellent results, compared with the regular test for bleaching quality, in all cases far more exact than is necessary at any time for technical purposes. If largely varying grades of pulps are to be determined, it is well, of course, to use correspondingly different standard pulps; for instance, one with 8, 12 and 16% bleach quality, although it is not absolutely necessary. I have been using many

times pulp with 6% capacity of bleaching as normal and have tested with it other samples which needed 14% bleach powder or more.

At last I might state that it may be possible to find some standard color solutions for different percentages, thus reducing again the time used for testing, although so far, experiments in this line have not been successful.   In the following table, some bleach tests are given and combined with a few of them, Hempel's nitric acid figure, the percentage of lignin, cellulose, etc.

Pulp Sample No	% Bleach powder New Method	% Bleach powder Old Method	Hempel's Nitric Acid Figure	% Ether Pitch	% Alcohol Pitch	% Water Extract	% Ash	% Lignin	% Cellulose
1	5,6	5,5	5,8	1,14	0,13	0,13	0,29	2,7	95,5
2	8,3	8,4	7,7	1,17	0,19	0,15	0,36	3,2	95,0
3	6,9	6,9	6,4	1,09	0,45	0,11	0,28	2,9	95,1
4	15,6	15,6	15,9	1,05	0,26	0,52	0,46	5,6	91,9
5	14,5	14,8		0,65	0,21	0,71	2,07	4,9	91,4
6	7,9	7,8	7,2	1,11	0,09	0,23			
7	7,3	7,3		1,03	0,12	0,27			
8	5,7	5,6		1,10	0,26	0,12	0,22		
9	6,1	6,2		1,06	0,17	0,11	0,28		
10	11,4	11,2							
11	13,8	14,1							
12	5,4	5,4							

These figures show in regard to the new and old bleach tests sufficient accordance to make the former one a suitable method for testing pulp in a short and simple way, and if it would be used only to prevent the enormous waste of manufacturing newspaper from high-grade pulp, it is serving one of its purposes.

NOTES ON COMMERCIAL DEXTRINS

By G. W. Rolfe

While the term "dextrin" is often used to designate a class of compounds of more or less definite composition formed by the transformation of starch whether hydrolytic or otherwise, the commercial products knows as "dextrins" are almost invariably made by roasting starch, which in many cases has been previously moistened with dilute acid, the heat being usually between 140° and 200° C. according to the qualities desired in the product. Only a few special "gums" which are classed as dextrins are products of a mild acid hydrolysis of water suspensions of starch after the manner of glucose manufacture.

From time to time covering a period of some years, I have carried on an investigation of these "torrefaction" dextrins with the object of learning more of their composition, particularly with reference to their relation to the products of acid hydrolysis.

In this work I have been assisted by my students, notably by the late George F. Ulmer and William White. The investigation has been frequently interrupted and is far from complete, but it seems appropriate to publish some of the work at this time.

Thirteen samples of commercial dextrins, supplied to us by a prominent manufacturer as typical products, were examined as to their behavior with iodine, optical rotation and cupric reducing power. No information was furnished as to the details of manufacture of these samples. In general, it is understood that "dextrins" are made by moistening the practically dry starch with dilute acid, preferably nitric, and roasting the mass at comparatively low temperatures, while the "British gums" are not treated with acid but roasted at a higher temperature. In the preparation of many of these dextrins, different characteristics are given by blending the more or less completely roasted products in varying proportions. Products of this latter class are usually more or less dark colored from the effect of the high temperature.

It is somewhat difficult to obtain solutions of many of these dextrins which are clear enough for polarizing. The treatment

which has seemed to work best is to bring the solutions to a boil, filter while hot and then rapidly cool the filtrate with running water.

The following table gives the results of the investigation of these thirteen dextrins:

TABLE I

ANALYTICAL DATA OF COMMERCIAL DEXTRINS

Name	I test	$[\alpha]^{D}386$	K_{386} (Dextrose—1.00)
1. German Std. Canary	Red	161.2	.0886
2. Superior Dextrin	Violet	174.0	.0342
3. German Std. White Potato	Wine red	176.6	.0778
4. German Std. Light Canary	Red Brown	156.5	.0673
5. White Potato	Wine red	181.8	.0832
6. German Dextrin	Red	169.4	.1508
7. Potato Canary		156.6	.0778
8. Tapioca Envelope No. 1	Brown	174.0	.0374
9. Envelope No. 2		166.2	.0562
10. Corn Dextrin	Brown	149.8	.0802
11. German Std. White Potato		177.1	.0840
12. Imported English Envelope	Brown Red	180.6	.0420
13. Imported German Potato Canary		154.3	.0733

It will be seen at once that these bodies, while showing iodine reactions and optical rotations like acid-hydrolysed starch products, have a very low copper reduction value. The plotted relations between specific rotation and copper reduction show no well-defined curve. As many of these commercial dextrins were probably mixed products, we next made dextrins in the laboratory under known conditions, applying as far as possible the fundamental principles of manufacture employed commercially.

Ten grams of potato starch were moistened with 3 cc. of dilute nitric acid (1 part of 1.44 acid in 100 cc. of water) and intimately mixed by rubbing with a pestle so as to obtain a homogeneous

RELATION OF SPECIFIC ROTATION TO CUPRIC REDUCTION

OF TORREFACTION DEXTRINS
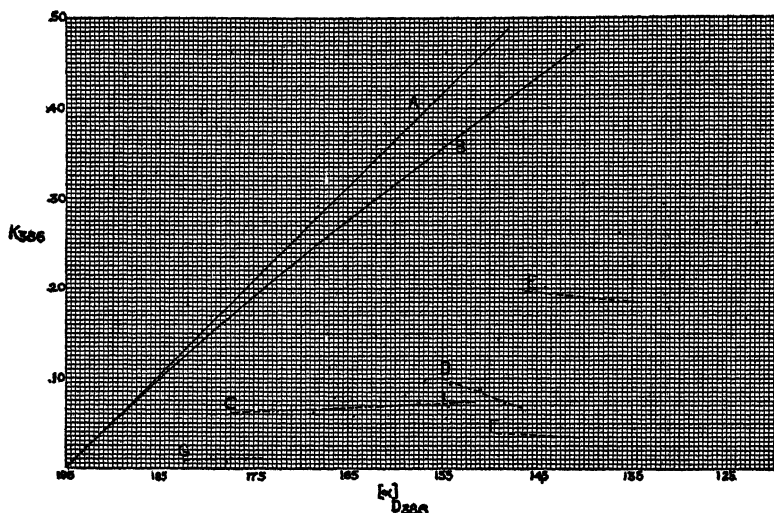
mass. The mixture was then spread out over the bottom of a flat
porcelain dish and heated in an oven kept at 110–115°. Iodine
tests were made on solutions of the dextrin produced.

The following are the results obtained:

Temp. = 115°

Time of Heating Minutes	Color with Iodine
0	Blue
15	Blue
30	Blue
45	Violet-blue
60	Violet
75	Red-violet
90	Rose-red
105	Red
120	Red-brown
135	Red-brown
240	Red-brown
300	Red-brown

TABLE II

OPTICAL AND REDUCING CONSTANTS OF DEXTRINE MADE IN
LABORATORY

Series I

(3 cc. of HNO³   Temperature = 110 – 115°C.)

Total Time of Heating (hours)	Specific Rotation $[\alpha]^D{}_{386}$	Cupric Reduction κ_{386}
3¾	168.7	.0614
2½	168.0	.0645
5	163.2	.0682
2¾	172.4	.0636
2	175.0	.0682
3	172.0	.0595
6	173.3	.0629
4¾	176.0	.0575
5¾	175.3	.0639
5	164.4	.0579
10	158.9	.0802
6	166.3	.0796
9	161.8	.0843
10	162.5	.0731
14	153.5	.0702
8½	157.9	.0501
14	154.4	.0696
16	158.6	.0573
23	156.9	.0979

Series II

(Heated with 6 cc. HNO₃)

5	151.1	.0862
13	148.4	.0730
6½	154.1	.0946

Series III

(Reheated 1½ hours with 3 cc. more HNO₃ added)

10½	136.5	.186
12½	141.5	.185
15	136.3	.202
12	144.2	.201

Series IV

(Reheated 1½ hours at 165° after previous heating with 3 cc. HNO₃)

Time Hours	Specific Rotation	Supric Reduction
9	148.4	.0385
6	147.0	.0369
20	142.4	.0351

Series V

(Heated without acid)

5	181.4	.0092
6	177.8	.0074
10	175.8	.0096
8	179.5	.0118
7½	179.1	.0123

These are the characteristic iodine colors shown by the transformations of starch and in the regular sequence of color change which marks the progress of acid hydrolysis.

The following investigations were then carried out: (1) A number of samples of potato starch were made up with nitric acid as described and heated for varying lengths of time at 110–115°. (2) Similar heat treatments were given starch mixed with double the amount of acid. (3) After heating for some time, samples made up as in (1) were treated with more acid and again heated. (4) Starch treated as in (1) was again heated at a higher temperature (165–170°) in an aniline bath. (5) Starch without acid treatment was heated to 165–170°. An investigation similar to that applied to the commercial samples of dextrins was made on these laboratory products and the results are tabulated below. (Table II). Plots of the relation of the specific rotation of these dextrins to their cupric reduction are also given.

Referring to this plot: Line A represents the relation between the specific rotation and cupric reduction of normal diastase-hydrolysed starch products; line B showing the same relation for normal acid-hydrolysed starch products. Lines C, D, E, F, and G show the corresponding relations of specific rotation to cupric reduction of the laboratory dextrins of Groups 1 to 5, respectively, and which are described above.

All these plotted values show that while the specific rotatory values decrease with continued heating, the cupric reduction remains practically constant. A study of these plots lead us first to the conclusion that probably a normal hydrolytic action begins on the starch, but very soon ceases owing to the evaporation of the hydrolytic agent, although a molecular change tending to a simplification of structure, as evidenced by the gradual diminishing of the specific rotation during the roasting as well as the corresponding iodine reactions proceeds continuously. That the slight cupric reducing power might be caused by normal acid hydrolysis seemed to be shown by the fact that in the Line G which represents products made by heating alone, after the manner of making the "British gums," the reducing powers are extremely slight as might be expected from the assumption that any hydrolysis proceeds simply from the action of moisture and weak acids originally present in the starch or produced by the heating. Starch treated with a larger proportion of acid, as shown in Line D, shows more reduction, as would be expected, although these results are not so pronounced as would be expected. This is partially accounted for in these samples by the fact that the volume of the acid solution was somewhat too large so that the starch was pasted slightly, preventing normal heat conditions throughout the mass. Line E shows the effect of adding more acid and reheating at 110–115° and indicates considerable hydrolysis. Line F showing products retreated with acid and reheated but at a higher temperature, shows a lower rotation but also a lower reduction. This is readily explained, however, as the product was highly colored, showing decomposition by the heating which would affect rotation and reduction alike.

An investigation was then carried out to learn more definitely whether the reduction value was actually caused by hydrolysis, and, further, what influence a more complete purification of the starch had upon the production of the reducing power in gums made by roasting starch without added acid.

As pure a starch as possible was made by treating a good quality of commercial potato starch with a 0.5% solution of potassium hydrate, keeping the granules in suspension by means of an air-blast. This treatment was continued for an hour, the starch then

allowed to settle and washed several times by decantation. The starch was then subjected to a similar treatment with a 1% hydrochloric acid solution, washing as before and then dried over sulphuric acid in a vacuum, 10 hours at 50°C. and then 20 hours at 100°. A test on the ash of the purified starch gave: 0.066%. Corn starch purified in the same way had 0.035% ash. The unpurified starches had, for potato, 0.21% ash, corn, 0.15%.

A preliminary roasting of two samples of the original potato starch and two of the purified, the samples being heated in copper vessels in an oil-bath at 156°C. and tested hourly, gave the following results.

Nos. 1 and 2 are the original starch, 1 being heated in an open crucible; 2 in a closed one; 3 and 4 being the same starch purified and heated in an open and a closed crucible, respectively.

IODINE TESTS

Time of heating	No. 1	No. 2	No. 3	No. 4
1 hour	Blue	Blue	Blue	Blue
2 hours	Blue	Blue	Blue	Blue
3 hours	Blue	Blue	Blue	Blue
4 hours	Blue	Blue-violet	Blue-violet	Blue-violet
5 hours	Blue	Blue-violet	Blue-violet	Blue-violet
6 hours	Blue	Blue-violet	Blue-violet	Blue-violet
7 hours	Blue	Blue-violet	Blue-violet	Violet
8 hours	Blue	Violet	Violet	Violet
9 hours	Blue-violet	Violet	Violet	Red-violet
10 hours	Blue-violet	Violet	Red-violet	Red-violet
11 hours	Violet	Violet	Red-violet	Deep red
12 hours	Red-violet	Violet	Red-violet	Deep red

These iodine tests, which were made on samples which had been boiled up with water and cooled, show the characteristic

changes in color of preliminary hydrolysis, the purified and anhydrous starch apparently showing more change than the commercial material which had about 10% or more of moisture. This is also shown in the following table of specific rotations and cupric reducing powers of the aqueous solutions of some of these samples:

(After 8 hours' heating)

Number	$[a]^D{}_{386}$	K_{386} (Dextrose = 1.00)
1	178.1	.015
2	176.5	.0117
3	172.9	.0002
4	169.1	.0169

(After 12 hours' heating)

1	174.5	.0246
2	174.8	.0219
3	171.6	.0163
4	162.1	.0314

Another series of heat transformations were carried out by the more effective arrangement of heating the starch spread in thin layers in flat dishes placed on shelves in a jacketed hot-air oven, kept at 165–170°C. by a thermostat.

These latter experiments were carried out with the intention of throwing some light on the effect of moisture on the formation of reducing substance.

Purified and commercial corn and potato starches were heated for different lengths of time and allowed to cool between successive heatings to absorb moisture from the air. Two batches of the commercial corn starch were then heated under similar conditions and one set cooled by being exposed to the air, the other in a vacuum dessicator between successive heatings.

The results are given in the following table:

Starch Sample	Time of total heating	Specific Rotation $[a]^P{}_{386}$	Cupric Reduction $^K{}_{386}$
Purified corn	4 hours	160.2	.0148
	6 hours	157.8	.0234
	8 hours	129.8	.0197
Com. Potato	4 hours	187.8	.0171
	6 hours	185.2	.0119
	8 hours	184.0	.0119
	11 hours	154.8	.0208
Purified Potato	4 hours	175.0	.0116
	6 hours	178.1	.0176
	8 hours	164.2	.0214
	11 hours	159.5	.0213
Com. corn exposed to air	2 hours	182.9	.0079
	3 hours	180.5	.0087
	5 hours	179.9	.0115
Com. corn cooled in vacuum	3 hours	185.9	.0118
	5 hours	178.4	.0111
	6 hours	173.1	.0176

It is perhaps premature to formulate conclusions from the data at hand. What has been established is that dry heat produces a cleavage of the starch molecule on lines similar to that caused by hydrolysis. Substances are formed which have a cupric reducing power of .01–.02 (dextrose = 1.00) but apparently they are not the result of any hydrolytic action of the moisture or acid bodies in the original starch, (see recent work of Malfitano and Moschkoff, Compt. rend., 154,443, in this connection) but may be due to a dextrose radical in the starch molecule which is included in the "stable" dextrin complex, as indicated in the work of Brown and Millar. (Jour. Chem. Soc., 75, 315).

It follows that those commercial dextrins showing reducing power more than .02 have been made by an acid treatment, the amount of acid used being indicated by the increase in reduction over .02, the time and degree of the heating being indicated by the specific rotation.

UBER HALBZELLSTOFFE

Von Carl G. Schwalbe

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Als Hauptbestandteile der Hölzer nimmt man Zellstoff-Lignin und Kohlehydrate an. Es muss beidem derzeitigen Stande der Forschung dahingestellt bleiben, ob die se Körper gruppen miteinander in chemischer Bindung sind oder nur ein Gemenge darstellen, ebenso was Lignin eigentlich ist. Unsere Aufschliessprocesse entfernen zum grössten Teil das Lignin und die Kohlehydrate also die "Nichtcellulose." Als Halbzellstoffe will ich nun alle diejenigen Zellstoffarten bezeichnen, die in ihrem Cellulose-bezw. Ligningehalt zwischen reinen Zellstoffen einerseits und Holz andererseits stehen. Je nach den angewendeten Verfahren ist diese Aufschliessung mehr oder weniger weitgehend. Wird mit heissem Wasser aufgeschlossen, wie es bis zu gewissem Grade beim Heissschliff geschieht, so steht das entstehende Produkt in seiner chemischen Zusammensetzung dem Holze noch ausserordentlich nahe. Voraussichtlich sind es kleine Mengen von Kohlehydraten die herausgelöst werden: denn *Klason* hat gezeigt, dass man durch heisses Wasser solche Kohlehydrate aus feinzerteiltem Holz herauslösen kann. Beim Braunholzschliff ist durch den Dampfprocess die Aufschliessung schon weiter gegangen, etwa 10–20% des Holzmaterials sind verschwunden. Der Cellulosegehalt des Braunschliffs weicht jedoch nach *Zacharias* von dem des Holzes kaum ab; man muss daher annehmen dass durch den Dampfprocess der Zellstoff des Holzes so verandert wurde, dass er zum Teil der Wirkung des Chlors bei der von *Zacharias* verwendeten Cellulosebestimmungsmethode von *Cross* und *Bevan* nicht mehr zu widerstehen vermag. Scheinbar hat also die Menge der Inkrusten eine Anderung nicht erfahren, wohl aber ist eine Veränderung der Art der Inkrusten nachweisbar. Braunholz liefert bei der Prüfung auf Phloroglucinadsorptions vermögen andere Werte als Holz den Zellstoffen ausserst nahestehend in Bezug auf Cellulose—besser auf Ligningehalt sind die Kraftzellstoffe. Auch hier zeigt sich wieder die Unmöglichkeit

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mit der *Cross* und *Bevan'* schen Chlorierungsmethode Unterschiede im Zellstoffgehalt zwischen normalen Natronzellstoffen und Kraftzellstoffen aufzufinden.   Auch heir mag die Ursache in mangelnder Widerstandsfahigkeit der durch den scharfen Koch-process geschadigten Natronzellstoffe liegen.   Sie werden vielleicht vom Chlor stärker angegriffen als die Kraftzellstoffe.   Ebenso wahrscheinlich aber ist es, dass nicht vorzugsweise die Menge der Inkrusten, sondern die Art der Inkrusten die Unterschiede bedingt.   Da sich auch im Ligningehalt (bestimmt durch die Phloroglucinadsorption keine Unterschiede zeigen, sind es wohl die Kohlehydratreste, welchen die verschiedene Festigkeit der Kraft—und Natronzellstoffe zuzuschreibar ist.   Die *Klason'* sche Ligninprobe, die Hydrolyse u. am. lassen gewisse Unterschiede der ganannten Zellstoffarten erkennen Theoretisch sind zwischen den Extremen: Holz und Zellstoff zahllose weitere Ubergangsstufen denkbar.   Gelingt es weitere solche Zwischenstufen festzuhalten, so sind wissenschaftliche und technische Erfolge zu erwarten. Wissenschaftliche Erfolge, weil das Studium der Halbzellstoffarten die bei Auflösung der die Faserbündel verkittenden Substanzen entstehen, Aufschlüsse über die Natur der Kittsubstanzen bringen kann.   Ein allmählich fortschreitender stufenweise gesteigerter Aufschluss wird am besten geeignet sein die Natur des Holzes zu entratseln.   Ich habe solche Studien begonnen.   Das bisherige wissenschaftliche Ergebnis ist, das die *verkittenden* Stoffe die Trager der Farbreaktionen auf Lignin sind.   Diese Reaktionen verschwinden schon wenn noch 80–90% des Holzmaterials vor-handen sind.   Die farbgebenden Stoffe treten demnach nur in relativ untergeordneter Menge auf; sie machen *nicht* die Haupt-menge des sogenannten Lignins aus.   Aus dem weiteren Abbau solcher Halbzellstoffe erhoffe ich allmahliche Entratselung des Lignins Technische Erfolge sind erzielt, wenn es gelingt den Faserverband des Holzes soweit zu lockern, das sich die Faser-bündel durch Kollergangarbeit unter Verlust von nur 10–20% seiner Menge in einen Brei aus verholzten Fasern verwandeln lassen, der auberordentlich zëhe feste Papiere ergibt, die je nach den Einzelheiten des angewendeten Aufschliessverfahrens saugend oder völlig leimfest sind.   Diese Papiere können in der Farbe des weiben Holzschliffes und dunkler Natronzellstoffe hergestellt

werden. Sie vergilben nicht oder nur sehr wenig. Sie werden
daher in den meisten Fallen reine Zellstoffpapiere ersetzen können
und bei Papieren aus Zellstoff und Holzschliff bedeutet der Ersatz
des Zellstoffs durch ein Surogat weitere Verbilligung. Denn bei
der Herstellung des Zellstoffs sind über 50% des Materials ver-
loren gegangen: bei der Herstellung des Surrogates nur 10–20%.
Weitere Vorteile ergeben sich, weil der Aufschliessprocess, eine
Modification des Sulfitkochprocesses, dem sich die bestehenden
Kochersysteme unschwer anpassen lassen schon in 3–6 Stunden
durchgeführt werden kann. Es labt sich demnach die Apparatur
weit stärker ausnutzen; auch ist der Warmeverbrauch weit gerin-
ger. Dis neuen Halbzellstoffe ergeben nach der *Cross'* schen
Chlorierungsmethode viel zu hohe Zellstoffzahlen für Lignin nach
der Absorptionsmethode aber ebenfalls. Diese Methoden lassen
sich also in ihrer gegenwärtigen Form nicht auf die neuen Halb-
zellstoffe anwenden. Wie schon erwähnt, reagieren sie mit dem
Phloroglucin-oder Salzsaurereagens nicht oder wesentlich sch-
wächer als Holz.

Das angewendete Verfahren gestattet auch Halbzellstoffe
herzustellen, die sich in ihrem Cellulosegehalt den üblichen Sulfit-
zellstoffen annahern, man braucht nur die Aufschliessdauer
entsprechend zu verlangern, bezw. die Concentration der aufschli-
essenden Flüssigkeit (einer Sulfitdauge) zu erhöhen. Es bietet
sich aber auch die Möglichkeit: anstelle des Aufschlusses durch
weitere langere Druckerhitzung, die von schädigendem Einfluss
auf die Festigkeit der Faser sein kann, die Aufschliessung ohne
Druck zu setzen. Schon *Kellner* hat versucht Holz mit eletro-
lysierten Kochsalzlaugen mit aber auch ohne Druck aufzuschlies-
sen. Der Electrolyse im Druckgefab vermochte die Apparatur
nicht zu widerstehen: die Elektrolyse ohne Druck verlangte feine
Verteilung des Holzes. Der erwahnte Halbzellstoff labt sich nun
da er als Faserbrei vorliegt, weit leichter aufschlieben als harte
Holzstücke. Es besteht also die Möglichkeit bei billiger electrischer
Kraft den Halbzellstoff durch die oxydierende Wirkung der
Hypochlorite bezw. Von Chlor und Alkali auf die Inkrusten in
Zellstoff zu verwandeln.

Das Aufschliessverfahren hat auch bei Holzabfallen nicht
versagt. Aus "Schwartenholz" konnte Halbzellstoff in gleich

hoher Ausbeute wie aus üblichem Zellstoffholz hergestellt werden. Aber nicht nur Holz allein, auch Stroh udgl. (Schilf usw.) erfahren Aufschliessung. Es ist eine verhaltnismässig geringfügige Abenderung des üblichen Aufschliessverfahrens mit Sulfiten, die zu den wie ich glaube, bemerkenswerten Ergebnissen geführt hat. Natürlich besteht auch die Möglichkeit durch modificierte alkalische Verfahren Ahnliches zu erreichen. Einige solcher Verfahren sind ja schon in Patentschriften beschrieben worden. Sie alle werden dazu beitragen, dass der bisherigen Verschwendung von Holzmaterial in etwas Abbruch getan wird, indem nicht mehr 50–60% sondern weit weniger des Holzes in die Ablauge gehen werden, ein vom volkswirtschaftlichem Standpunkte aus hochbedeutsames Ziel.

ANALYSE DU PAPIER (DOSAGE DES FIBRES)

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Il est connu que lorsqu'on examine un papier sous le microscope certain réactif tels qu'une solution de iode dans de l'iodure de potassium et dans le iodure de zinc nous rendent des grand services en faisant distinguer les differentes fibres dont se compose le papier par la différence de coloration donnée aux fibres par les réactifs. Il est souvent très difficile de reconnaître les fibres d'après leur forme car elles sont dans le papier dechirées et déformées. J'ai trouvé qu'avec au peu d'expérience on peut reconnaître les différentes fibres du papier par les colorations diverses que donnent les dits réactifs et sans avoir recours au microscope; ce qui est très pratique. Cette methode donne en général de bons résultats; elle est très expeditive et pratique surtout lorsqu'on ne dispose pas d'un bon microscope ou en voyage losqu'on veut vite s'assurer de la composition du papier. Il est clair que lorsqu'il s'agit de papiers très compliqués, l'examen ne peut être fait sans l'aide du microscope. Si par hasard le papier contient de l'amidon il faut le traiter a l'eau chaude acidulée pour l'en débrasser.

J'emploie les solutions, dont on se sert pour distinguer sous le microscope des différentes fibres par leur coloration au contact des dites solutions. Quoique la préparation de ces réactifs est connus je l'indique toute de même.

I. Solution de iode au iodure de potassium.

Eau	20 cm.^{3}
KI	2 gr.
I	1,15 gr.
Glycerin	2 cm.^{3}

II. Solution de iode au iodure de zinc et de potassium. On prépare d'abord une solution de 20 gr. $ZnCl_2$ en 10 cm^3 d'eau, puis une solution de 2,1 gr. de KJ et 0,1 gr. 1 dans 5 cm^3 d'eau. On mélange laisse réposer et décante le liquid claire.

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III.   Solution de iode au chlorure de magnesium. 50 cm³ une solution saturée de MgCl₂ et 2,5 gr. de la solution *I*.

IV.   Solution de phloroglucine.

On dissout 1 gr. de phloroglucine dans 50 cm³ d'alcool et on ajoute 25 cm³ d'acide chlorhydrique.

Voici comme on procéde pour obtenir des réactions.   On fait tomber une goutte de la solution *I* et de la solution *II* sur le papier examiner et on laisse réagir chaque solution pendant 20-25 secondes, puis on lave avec de l'eau, en faissant tomber une goutte d'eau, puis on observe de quelle façon la tache change la couleur ou comment elle se décolore plus ou moin vite.   La solution *I* réagit plus vite que la solution *II*.   (La solution *III* ne s'emploie que lorsque les premières deux solutions ne sufficent pas à reconnaître la nature de la fibre.)   Ainsi les chiffons se décolorent plus lentement que la cellulose.

Je me suis aussi occupé de fibres rarement employées chez nous et qui au Japon servent à la fabrication du papier qui est de plus en plus importé au Europe.

Lorsqu'il s'agit de papiers très compliqués avec diverses fibres, des déchets, etc.; il faut tout de même avoir récours au microscope mais ces cas sont rares et en géneral ma methode permet de vite reconnaître la composition du papier.   Si le papier contient de l'amidon il faut l'en débarasser en le lavant à l'eau chaude accidulé légerement à l'acide chlorhydrique.   Il arrive aussi que deux sortes des fibres donnent la même réaction lorsqu'elles sont soumis au même réactif, il faut alors essayer un autre.   J'ai examiné les réactions de papiers contenants les fibres suivantes: cellulose de bois crue et blanchie, cellulose de paille, esparto kodzu, missumata, gampi lin, coton, bois, bambou.   Voici la liste de la coloration des taches faites sur ce papier examiné à l'aide des réactifs.

Fibres simples.   Coloration avec la solution I + KI.

Le papier se colore *en brun violet:* Kodzu lavé avec de l'eau la couleur devient d'abord rouge, puis passe an bleu d'indigo.

Le papier se colore *en jaune brunâtre: Misumata* lavé devient olive pouis jaune verdâtre.   *Gampi* en peu plus foncé que missumata.   *Bambou* lavé devient *jaune*.   *Pâte* de bois se recconait aussi au phloroglucine.

Le papier se colore *bruntabac: Lin,* au lavage brun clair, les bords bleus. *Coton* au lavage devient bleu. *Cellulose* (blanchie) coloration olive pale pois decoloration complète. *Pâte de bois* (brune) après lavage violet sale.

Le papier se colore *brun rougeâtre: Cellulose* (brute) au lavage comme la cellulose blanchie. Cellulose de paille au lavage plus claire qui la cellulose de bois blanchie.

Le papier se colore *jaune clair:* Pâte de bois pure.

Le papier se colore *violet presque noir:* Esparto au lavage violet bleu foncé de petites taches noires qui persistent longtemps.

Réaction par la solution I = Zn I.

Coloration violet brunâtre: Cellulose de bois blanchie. Cellulose de bois brute. Les deux se décolorent très vite. *Cellulose de paile* se décolore plus lentement.

Coloration bleu violet quelquefois très foncé: Kodzu lavé passe au violet et devient *bleu* (cellulose et lin se décolore au violet claire) (lin et coton se décolore lentenment). *Gampi* lavé passe au gris et se décolore complètement.

Coloration violet rouge: Esparto pâlit au lavage puis devient gris bleu avec les taches foncées.

Coloration gris bleuâtre: Pâte de paille se décolore en jaune très claire.

Coloration gris brunâtre: Pâte *de bois* (noir avec la phloroglucine).

Il est quelquefois difficile de distinguer deux espèces de fibres une à coté de l'autre, quelquefois on distingue facilement trois différentes fibres dans le papier selon leur espèce. Voici quelques exemples: Chiffons mêlés à la cellulose de bois. Plus il y a de chiffons plus la coloration avec I + IK (Solution *I*) est brun tabac foncé, si outre les chiffons le papier contient aussi la cellulose de paille la coloration est encore plus intense. Plus le papier contient des chiffons plus la décoloration est lente et teinté en oliv, ou en gris. S'il contient peu de chiffons la décoloration est brun rouge. On distingue le coton du lin à ce que le lin reste brun violet après le lavage, tandisque le coton devient et reste bleu, un peu olivâtre. Si les chiffons mixtes se trouvent avec de la cellulose il est difficile de les distinguer à moins ne soit en petite quantité. Pâte de bois et cellulose se colore en jaune-brun et se décolore en jaune claire

très vite, mêlé à des chiffons la couleur reste bleue. Les bord et le milieu de la tache deviennent olive. La présance de la pâte de bois se reconnait à l'aide de la phloroglucine. Si avec la pâte de bois se trouve de la cellulose de bois brute ou obtient une coloration brune orange, qui après être lavé prend une teinte jaune: *Cellulose de bois et de paille* — Coloration brun-rouge, plus il y a de la cellulose de paille plus la coloration tire sur le rouge, qui après le lavage devient clair. Les fibres qui se trouve us dans les papier japonais se comportent ainsi. Kodzu et mitsumata se colorent en brun havanne; plus on moin foncé quelquefois en brun très foncé. La décoloration est olive et partielement brune. Kodzu et mitsumata se color en brune, lavé devient vert jaunâtre. Lorsqu'on n'arrive pas a déterminer éspèce de fibre au moyen de la solution I KI + I on examine le papier au moyen de la solution (II)I ÷ Zn I. Par ce réactif les chiffons melés à la cellulose donnent coloration violet (*bleu*) foncé qu'au lavage passe au violet bleuâtre et reste violet clair a la fin. Pour les chiffons de coton la tache devient plus grise après la décoloration tandisque pour les chiffons de lin elle passe plutôt au violet. Le papier fait avec pâte de bois et cellulose blanchie devient violet et se décolore jusqu'à une teinte jaune-clair, s'il contient aussi des chiffons la couleur passe à l'olive au lavage. Kodzu et mitsumata se colorent en violet de fer (comme la laque d'alizarine au fer) et au lavage devien ent d'abord vert bleuâtre puis gris. Kodzu et gampi réunis donnent la même coloration. Gampi et mitsumata se colorent en violet-sale au lavege pour passer ensuite au violet-clair puis à la fin au gris bleuâtre. Voici la table des résultats des réactions obtenues sur des papiers fabriqués avec diverses matières premières.

Espèce de fibre	KI + I	KI + I après le lavage	ZnI + I	ZnI + I après le lavage	Remarque
Cellulose de bois ordinaire.	Coloration brune	Passe a l'olive tirant ensuite sur le brun.	Violet brunâtre	Se décolore assez vite en passant d'abord au gris.	
Cellulose de paille blanchie.	Rouge brune clair plus que la cellulose de bois.	Devient p l u s claire.	Violet	Devient grise puis se décolore tout à fait.	
Cellulose de bois blanchie.	Brun-rouge.	Pâlit devient olive très clair.	Bleu-violet	Se décolore assez vite en passant d'abord au gris.	
Pâte de paille.	Brune tirant en peu sur le rouge.	Se décolore lentemente devient brun-clair.	Coloration grise.	Se décolore vite en un jaune très clair.	
Pâte de bois.	Brun-clair jaunâtre.	Devient plus clair mais garde la même nuance.	Gris tirant sur le brun.	Devient j a u n e clair (chamois).	Coloration rouge au phloroglucin.
P â t e d e b o i s brune.	Brune.	Devient p l u s clair.	Brun-violet foncé.	Devient un violet pâle.	
Bambou.	Jaune brunâtre.	Passe au j a u n e franc.	Violet-gris b l e u.	Se décolore tout à fait.	

Espéce de fibre	KI + I	KI + I après le lavage	ZnI + I	ZnI + I après le lavage	Remarque
Lin chiffons de lin.	Brune.	Brun-claire bords bleus.	Violet-brunâtre.	Se decolore lentement.	
Coton chiffons de coton.	Brune.	Devient bleu.	Violet-bleu.	Se décolore lentement.	
Kodzu.	Brune tirant sur le violet.	Violet foncé, puis indigo.	Violet-bleu foncé presque noir.	Devient plus clair à la fin *bleu*.	
Gampi.	Brune havana plus foncé que mitsumata.	Olive puis v e r t jaunâtre claire.	Violet franc foncé plus foncé que mitsumata.	Se décolore vite complètement.	
Mitsumata.	Brune havane.	Olive c o m m e Gampi mais en se décolorant ne fournisent pas un si franc vertjaune.	Violet bleuâtre.	Devient facilement violet-claire puis gris verdâtre.	
Lin et coton.	Brun foncé.	Bleu-violet.	Violet.	Reste bleu violet à la fin devient gris.	

Espèce de fibre	KI + I	KI + I après le lavage	ZnI + I	ZnI + I après le lavage	Remarque
Coton et cellulose blanche.	Se décolore très vite en brunrouge.	Se décolore plus lentement que la c e l l u l o s e meme reste olive brunâtre.	Violet de fer comme la liquide d' alizarine et de fer.	Se décolore en gris.	
Lin, coton et cellulose blanche.	Rouge-brune.	Bleu-brun violet.	Violet.	Bleu-gris.	
Lin et cellulose blanche.	Brun tabac foncé.	Passe au violet foncé et reste violet.	Violet.	Passe au violet bleu et reste violet clair.	
Chiffons et en peu de cellulose.	Brun tabac.	Bleu-violet.	Violet.	Bleu.	
Chiffons et pâte de bois.	Brun-rouge.	Devient clair le bord bleu.			Rouge au phloroglucin.
Pâte de bois. Cellulose de bois ordinaire.	Jaune. Brunâtre.	Jaune-clair.			Rouge au phloroglucin.
Pâte de bois. Cellulose blanchie.	Jaune. Brunâtre.	Jaune-clair.	Violet.	Se décolore en jaune-clair.	Rouge au phloroglucin.

Espéce de fibre	KI + I	KI + I après le lavage	ZnI +I
Cellulose chiffon Pâte de bois.	Jaune. Brunâtre.	Jaune-clair.	Brunâtre.
Cellulose de bois. Cellulose de paille.	Brun-rouge.	Olive-claire.	
10% chiffons. 90% cellulose.	Brun-tabac.	Devient olive brun les bords bleu.	Violet.
20% chiffons. 80% cellulose.	Brun-rouge claire.	Passe à l'olive. On remarque long-temps des fibres bleus.	Violet.
95% chiffons. 5% cellulose.	Brun tabac foncé	Bleu-clair.	Violet.
70% cellulose de bois. 15% chiffons. 15% pâte de paille	Brun foncé vio-lacé.	Bleu-violacé. Reste longtemps.	Violet pure.

Espéce de fibre	KI + I	KI + I après le lavage	ZnI + I
50% chiffons. 15% cellulose de paille. 35% cell. de bois.	Brun foncé presque noire.	Bleu franc.	Violet foncé
30% chiffons. 15% cellulose de paille. 55% cell. de bois.	Brun foncé.	Bleu-sâle.	Violet-brun.
50% cellulose. 50% chiffon.	Brun-tabac.	Se décolore lente-ment le autre ol-ive les bords gris-bleu.	Violet.
45% cellulose de bois. 45% cellulose de paille. 5% chiffons.	Brun-violet.	Jaune-claire. Verdâtre. Verdâtre.	Violet.

Zn1 + I après le lavage	Remarque
Passe à olive, puis se décolore complètement.	Avec Mg. Cl₂ violet brun lavé devient à la fin jaune.
	Mg. Cl₂ rouge.
Bleu-clair.	
Se décolore vite mais toute demeine plus lentement que la cellulose pure.	
Se décolore lentemente.	
Violet-bleuâtre.	

ZnI + I après le lavage	Remarque
Violet-bleuâtre.	
Violet bleu puis gris.	
Gris-violacé.	
Jaune-claire.	Par Mg. Cl₂, rouge tirant sur brun, lavé devient jaune pur gris verdâture.
Verdâtre.	

Espèce dç fibre	KI + I	KI + I après le lavage	ZnI + I	ZnI + I après le lavage	Remarque
50% cellulose, 40% pâte de la.	Brun-tabac.	C o u l e u r olive, bords gris bleu-âtres.	Violet de fer.	Gris-bleuâtre.	Phloroglucin rouge.
Papier d'alfa (es-parto).	Violet foncé presque noir.	Violet blue indigo, petites tâches noir.	Violet-noir.	Passe au bleu puis gris les tâches indigo restent longtemps.	
Papier Romeo $\frac{1}{3}$ chiffons, $\frac{1}{3}$ cellu-lose de bois, $\frac{1}{3}$ esparto.	Brun-foncé.	Reste long-temps brun puis olive brunâtre.	Violet foncé.	Se décolore lente-ment reste vio-let brun tâches foncé.	
Kodzu et mitsu-mata.	Brun-havane pur.	Olive parci et par la brun.	Violet de fer.	Verd bleuâtre à la fin gris.	
Kodzu et Giampi.	Ainsi quele précedant.				

BREEDING MAIZE FOR INDUSTRIAL PURPOSES

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No other agricultural crop is made to serve such a variety of purposes as Indian corn. The long list of products and by-products manufactured from the grain as well as from other parts of the plant is ever increasing. In view of this fact is suggested the idea of adaptation by altering the physical structure or the chemical composition, as the case may be, of the various plant parts involved in order to better serve the varied and special needs.

In those industries utilizing the grain, starch is of course usually the basic product sought. This starch is either refined and sold as such, or it is converted into some of its transformation products such as glucose, alcohol, gum, dextrin, etc. Upon first thought, therefore, one might suppose that a variety of corn high in starch content would be the most desirable kind for these industries. But the case is not so simple as would appear on first thought for with the great development of by-products in these industries within recent years conditions are entirely changed. For example, the protein compounds have found an important place on the market on account of the demand for these by-products for feed-stuffs. Perhaps the most striking development of such a by-product is the corn oil. In former years the germs which contain the bulk of the oil were a waste product. Now such is the demand for the oil of corn that this substance has become pound for pound much more valuable than the starch itself. According to present market reports corn oil is quoted as being worth more than three times as much as corn flour.

In view of these facts it will be seen that no one kind of corn will be suited equally well to all the corn industries but that each industry may demand a sort adapted to its own particular needs which indeed may even vary from time to time according to market demands.

It is interesting, therefore, in this connection to know in what manner and to what extent corn may be influenced as to its composition.

Sixteen years ago the Illinois Agricultural Experiment Station began some experiments to answer these questions. It was already established that the composition of grain could be affected to some extent by environment. The case of the sugar beet stood as a classic example of what might be accomplished in changing the composition of a plant part by directing the forces of heredity. So far as known, however, the matter of breeding to influence the composition of a grain by selection was a new proposition.

It was necessary, therefore, to work out first methods of selection and then plans for propagating the breeding plots.

In taking up the investigation it was proposed to take a variety of corn and to select in four different directions, as follows:

First, a strain was selected to increase the protein content, the practical consideration in this case being from the nutrition standpoint.

From the same original lot a second strain was selected for a low protein content. Low protein, of course, means high starch and in such a corn we would have theoretically a kind well adapted for distilling purposes.

In another strain high-oil content was the object sought, making of this a valuable corn for the glucose and allied industries in which the oil output forms such an important product.

Finally a low-oil strain was started chiefly for the purpose of comparison. Incidentally, however, a kind of corn with a reduced oil content would be of advantage in feeding hogs for the finest quality of bacon and lard.

The corn chosen for carrying out these experiments was an ordinary white variety grown in central Illinois and then known as "Burr's White." Its original composition was as follows:

Protein.............. ..... 10.92
Oil 4.70
Ash 1.43
Carbohydrates 82.95

Selecting by chemical analysis those individual ears whose content was found to be best suited to the various purposes, and breeding in separate and isolated plots each group by itself, four strains were gradually evolved which have finally developed into quite different kinds of corn so far as chemical composition of the grain is concerned.

Naturally the results have been affected more or less by environmental agencies. Thus there have been fluctuations due in part to soil and season, which influences it has been impossible to entirely eliminate from those due to heredity.

In order to obtain a brief comprehensive view of what has been accomplished in these experiments up to the present time, perhaps we may best compare the analyses of the four strains in the crop of last year (1911), after 15 years of breeding, with the original variety in 1896 from which they emanated.

In doing so, however, we should bear in mind the above statement concerning seasonal fluctuations and consider that we have represented in these data the results of a single season which might have been slightly modified in another kind of a season.

Following are the results of the protein breeding:

PROTEIN CONTENT, DRY BASIS

Original Variety, Crop of 1896...... 10.92 per cent
High-Protein Strain, Crop of 1911.. 13.78 per cent
Low-Protein Strain, Crop of 1911 ..   7.89 per cent

It may be noted here that the figures given above for the composition of the original variety represent fairly well the average composition of ordinary dent corn.

Since in the percentage composition protein and starch are complementary, it appears that we have now in this high-protein strain a sort of corn that contains about $1\frac{1}{2}$ pounds less starch per bushel than ordinary corn, while the low-protein strain would furnish a corn about $1\frac{1}{2}$ pounds per bushel richer in starch than average corn.

The progress in breeding to influence the oil content is shown in similar manner in the following results:

OIL CONTENT, DRY BASIS

Original Variety, Crop of 1896...... 4.70 per cent
High-Oil Strain, Crop of 1911...... 7.51 per cent
Low-Oil Strain, Crop of 1911........ 2.05 per cent

Thus we see that breeding has produced in the high-oil strain a kind of corn that now contains almost $1\frac{1}{2}$ pounds per bushel more oil than exists in average corn, while on the other hand breeding for low oil has caused a reduction in this constituent amounting to about $1\frac{1}{3}$ pounds per bushel. Since there exists a correlation between oil and protein this last strain is correspondingly richer in starch.

It may be said that these experiments are still being continued and it is possible that even wider limits may be reached in some directions. These results serve to indicate something of the possibilities for improvement along these lines.

Very little has been done in improving economic production in our corn industries through chemical control of the raw product. The sugar beet stands as the classic example of the adaptation of a plant by the strenuous control of its chemical composition. In Europe considerable attention is given to the adaptation of the potato with reference to its starch content for distilling purposes, and special stress is laid upon the matter of composition of barley in its application to the brewing and distilling industries.

Doubtless vast possibilities exist for improvement in economic production in our corn industries in this very matter of the adaptation of corn to meet the special requirements by breeding for special industrial purposes.

THE CONSUMPTION OF CAUSTIC SODA IN COOKING WOOD AND THE INFLUENCE OF THIS CONSUMPTION ON THE YIELD AND BLEACHING PROPERTIES OF THE FIBRE PRODUCED

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In spite of the many years which have elapsed since the introduction of the soda process for cellulose manufacture, it is still run largely by rule-of-thumb methods. It is, for instance, known in a general way that increasing the time of cooking, the amount of caustic, or the steam pressure will diminish the yield, but the exact relation of these three factors has, so far as we have been able to discover, never been worked out. Another point on which no information was available was the consumption of caustic soda in cooking wood and the influence of this consumption on the yield and bleaching properties of the fibre produced. As it seemed desirable to obtain this information a series of cooks of poplar wood was made with this object in view.

The wood used was in the form of the regular chips employed in pulp mill practice, and consisted almost entirely of two species of poplar, Populus tremuloides and P. grandidentata. The cooks were made in two ways; those in which less than 10% of caustic was used being digested at about 95° C. in a copper flask fitted with a reflux condenser, while those with over 10% of caustic were cooked in a small rotary digester heated by a gas flame. At the end of each cook the black liquor was sampled, the fibre washed and its yield carefully determined.

The black liquor was analyzed in the following way. To 300 cc. of water containing 15 cc. of barium chloride solution (400 grams per litre) there was added from a pipette 25 cc. of the black liquor. This was then titrated with normal acid and the end point determined by removing a drop at intervals and allowing it to fall into a thin layer of dilute phenolphthalein solution contained in a beaker. When the drop no longer produced a pink color the

reaction was considered complete. A second test was then made by evaporating 25 cc. of the black liquor to dryness, burning off the organic matter and titrating the soda ash present with normal acid, using methyl orange as an indicator. The relation of these two tests gives the causticity of the black liquor and by comparing this with the causticity of the original cooking liquor the amount of caustic used up in the process can be readily calculated.

The results of the entire series of cooks are shown in chart A in which the total yield, whether of good fibre or of merely softened chips, is plotted against the caustic consumed. Both of these are expressed in percentages based on the bone-dry wood used. The starting point of this curve is taken as the yield obtained when finely divided chips are extracted with water at 95° C. till the extract is colored only very faintly yellowish. This chart also shows a curve plotted in the same way from the results of a few cooks of spruce chips. It is seen that in a general way the reactions follow the same course, though the slight divergence of the upper portions of the curves seems to indicate that the celluloses being acted upon are different in their composition.

A study of the curve for poplar shows that between the points of 14 and 19.5% caustic soda consumption the relation between the yield and the caustic soda used up is not so definite as it is beyond these points. This may perhaps be due to the fact that within this range the transition from chips to fibre takes place while below 14% and above 19.5% it is practically all chips and fibre respectively. It is seen that the reaction taking place up to a consumption of 15% of caustic is quite different from that above this point. This probably indicates that in the first portion of the cook the non-cellulose constituents of the wood are being dissolved most rapidly, while after 15% of caustic has been used up the residue is as nearly pure cellulose as the process will yield and from this point on is dissolved as a whole. There is, then, little to be gained, so far as the purity of the product is concerned, by making the cooking conditions severe enough to use up more than 15% of caustic soda. It is, however, quite probable that the additional cooking would impart to the fibre certain desirable physical qualities which would not be in evidence in the less drastic cooks.

CHART A.

Poplar.

Spruce.

Percent Total Yield.

Percent NaOH Consumed.
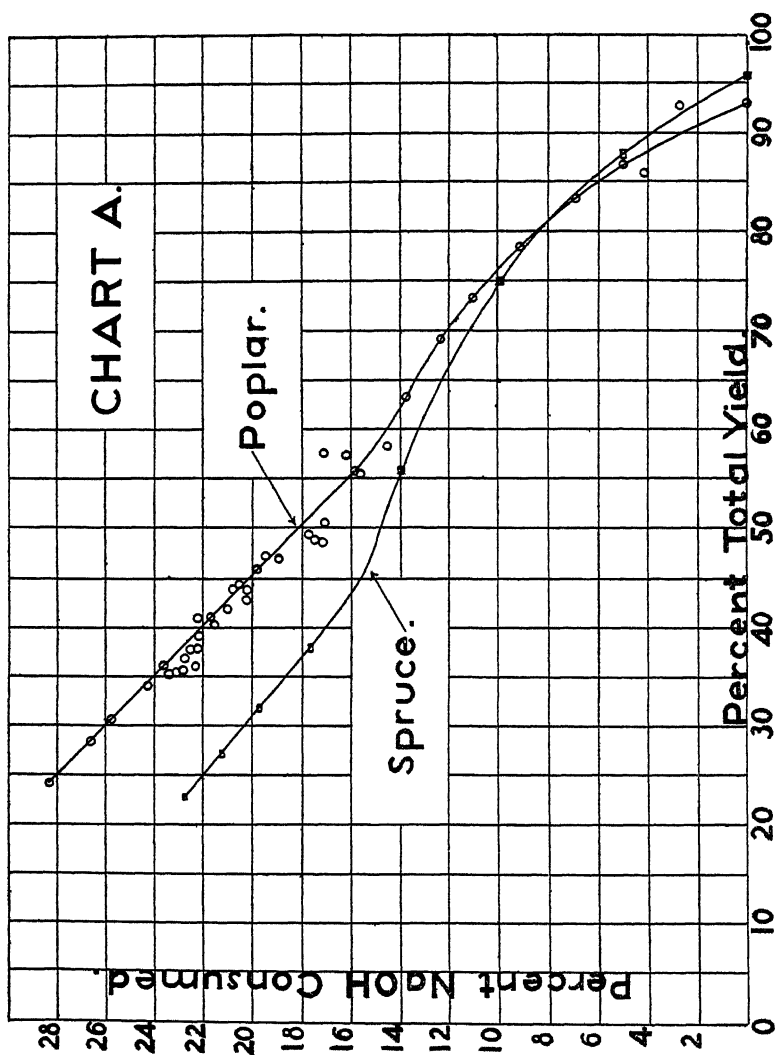
In each of the cooks in which the chips were sufficiently acted upon to produce fibre a study was made of its bleaching qualities in connection with the caustic consumed, the strength of the solution at the end of the cook and the percentage of residual caustic based on the bone-dry wood.   It was expected that the bleach required would depend very largely on the amount of caustic consumed but it was proved that all three of the above factors could be varied within quite wide limits without appreciably changing the amount of bleach required.   Thus fibre bleaching with about 7% of bleach was produced in cooks where the consumption of caustic varied from 20 to 25%, the residual caustic from 3.5 to 8%, and the strength of solution at the end of the cook from 8 to 22 grams per liter of caustic soda.   It appears to hold true that a low consumption together with a slight excess of caustic will give a hard bleaching fibre while if the excess is greater the fibre will bleach easier even if the consumption of caustic is the same or slightly less.

It is highly probable that the bleaching properties of the fibre depend on certain definite combinations of the three factors mentioned, but the data available are not sufficient to determine positively the laws which govern the results.

In considering the curves shown on chart A it is to be noted that the points plotted were determined under very widely varying conditions of treatment.   Thus the steam pressure has varied from 70 to 130 lbs., the caustic added from 22 to 50%, etc., yet the yield seems to be perfectly definite for any given consumption of caustic regardless of how this consumption was caused to take place.   This fact, taken in connection with the slight variations in bleaching properties of fibre produced under such different conditions, leads to the conclusion that in the cooking of wood the important point is to use up a definite percentage of caustic and that so far as the character of the product goes it is apparently immaterial whether this consumption is caused by time, temperature, strength of cooking liquor or any other factor.

It should, therefore, be possible to ascertain the condition of the stock in the digester at any time by making an analysis of the black liquor, and thus avoid over-cooked or under-cooked fibre. The chief reason why this cannot be done at present is the

length of time necessary for the determination of the total soda in the black liquor. If a rapid and accurate method could be devised for this test it is thought that this manner of following the progress of the cook would prove very valuable in the soda process.

In conclusion I wish to acknowledge my indebtedness to S. D. Warren & Co., in whose laboratory this investigation was carried on, and to my associates for much valuable assistance in obtaining the original data.

Abstract

[ON THE CHEMICAL COMPOSITION OF WHITENED RICE, WITH ESPECIAL REFERENCE TO THE NUTRITIVE VALUE OF ITS PROTEIN MATTERS FOR SAKE YEAST AND ASPERGILLUS ORYZAE

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The chemical analyses of whitened rice hitherto published have, in all the cases, been limited to those made upon ordinary samples. The authors have analyzed samples of rice which were specially prepared for the purpose of brewing saké, namely, those which were whitened in the highest degree. They were 44 in number and collected from 22 breweries, which are located in different parts of Japan.

After determining the general chemical composition of these samples and discussing the results, the authors proceed to the examination of protein matters, of which they have isolated albumin, globulin, prolamin and oryzenin. The existence of prolamin, a protein with bitter taste and soluble in 80% alcohol, in rice is worthy of remark, inasmuch as Rosenheim and Kajiura, in their examination of rice, failed to detect any protein soluble in alcohol, and Osborne states that the absence of prolamin in rice is an exception to the general rule that all the cereals examined in his laboratory contain prolamin. There is, therefore, reason to doubt the correctness of the observations made by Rosenheim and Kajiura. Elementary analyses of the proteins thus isolated from rice showed, however, small differences in their composition as compared with the composition of those contained in other cereals and determined by Osborne, Ritthausen, Chittenden and others, the essential differences in the case of prolamin being that the percentage amount of nitrogen in the protein obtained from rice is somewhat below that contained in other cereals.

Further, the authors have examined the nutritive values of the four proteins obtained from rice for saké yeast and Aspergillus Oryzae, and the results show that the albumin, the globulin and the orizenin are all and equally well assimilated by these organisms whilst the prolamin is not in the least utilized by them.

THE CARBOHYDRATES OF WHEAT AND WHEAT PRODUCTS AND CHANGES IN SAME DURING DEVELOPMENT OF THE GRAIN

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During the summers of 1897 and 1898, while the writer was chemist of the Arkansas Agriculture Experiment Station at Fayetteville, Arkansas, he collected samples of wheat on each succeeding day from the first formation of the grain until several days after it was ripe and fit for harvesting. The purpose of collecting these samples was to determine changes in composition both with regard to the nitrogenous matter and the other constituents. ' Determinations as to the composition of the nitrogenous matter were made on each individual sample of wheat collected. For the other determinations the cuttings of each three days were mixed and the analyses were made on these mixtures. The mixtures are designated by groups in numerical order. Groups V and VI represent the wheat in the milk when gathered, — Group X at about the average time of cutting.

The results of the first year's work were published in detail in Bulletin No. 53 of the Arkansas Agriculture Experiment Station in September, 1898. The results of the second year's experiments have not previously been published. Much of the analytical work for the latter experiments was completed by Mr. J. F. Moore and supplied to the writer after he had left the Experiment Station in 1899. The analyses of flour, germ and bran were made recently at The Columbus Laboratories, Chicago.

There are three distinct parts of· the wheat grain, — the bran, the embryo or germ, and the endosperm or portion which yields the flour. During the milling operations in most mills the germ and bran, with some portion of the endosperm, find their way together into the offal which is usually sold as feed for animals. In some of the larger mills the germ is separated in a nearly pure condition so that with a little care it can be obtained in a fair de-

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gree of purity.   The sample of germ of which the analysis is here given was freed as completely as possible from flour and bran and was fairly pure.   It contained, however, some flour which was pressed into it during the process of flattening the germ in the milling operation.   This accounts, at least in part, for the starch found in it.   Patent flour, such as was used in this series of analyses, contains neither bran nor germ.   The starch in the bran comes largely, if not entirely, from flour which was not removed during milling.

There is a distinct connection between the composition of the three parts of the wheat berry and the composition of the wheat at different periods of its growth because there is a marked difference in the rate of development of the different parts of the wheat berry in the process of its growth.   Especially is this true concerning the bran and endosperm, for the proportion of bran to endosperm is much greater in the smaller and immature kernels than in the fully ripened and plump grain.

The method of analysis used for the determinations on the carbohydrates is given below.   The method of determining the other constituents is the same as outlined in the official methods for food analyses, excepting that the amides were determined by precipitating all proteids and albuminous matter from the water extract by the use of phosphotungstic acid and determining the amide nitrogen in the solution.   This method has been found to be preferable to the use of cupric hydroxide, for wheat products. In the table of analyses the actual proteins are given and were obtained by multiplying the actual protein nitrogen by the factor 5.7, which is the true factor for wheat proteids.   The amides were found by multiplying the amide nitrogen by the factor 5. This factor is based on the average composition of the amides, asparagine and glutamine.   For convenience of reference both the total and amide nitrogen are also given in the table.

Pentosans: These were estimated by the current method of the Association of Official Agricultural Chemists, which is distilling with hydrochloric acid to convert them into furfural, precipitating the furfural with phloroglucin and computing the results as xylan.

Sugars: To determine the sugars, two grams of meal were

extracted with hot, strong alcohol. This was distilled off and the sugar extracted from the residue with water. In the solution thus obtained the reducing sugar was determined by Allihn's method. In another similar extract the total sugar was determined by inverting the sucrose in the water solution with hydrochloric acid, neutralizing the acid with sodium carbonate and then proceeding as before. The difference in the reducing power of the extract before and after inverting gave figures for computing the sucrose.

Starch: The hot alcohol extracts not only the sugars, but also the greater part of the fat. The residue is therefore in a suitable condition for determining the starch by the diastase method. This method was carried out according to details adopted by the Association of Official Agricultural Chemists, except that instead of boiling the acidified solution for two and one-half hours the flasks containing the liquid were immersed in a steam bath for three hours. The temperature in this bath was very nearly that of boiling water, and the method has been found convenient and satisfactory. The resulting sugar was determined by Allihn's method. The results include starch and dextrins. The dextrins being determined, the starch is found by difference.

Dextrins: It was found that extracting the meal with hot 92 per cent alcohol converts a portion of the starch into a form soluble in cold water and a separation of the dextrin from this portion of material is impracticable. Accordingly, to determine the dextrins, five grams of the fresh material were thoroughly digested in a 250 cc. flask with cold water; 200 cc. of this clear filtered extract were treated with hydrochloric acid in the steam bath in the same manner as the diastased starch solutions. The reducing power of the resulting solution is due to sugars and dextrins. The reducing power of the sugar having been determined, the dextrin compounds are computed from the difference.

In the tabulated results of the series of analyses on wheats out at different dates, the amount of starch and undetermined is given as found by difference. No determination was made of the actual amount of starch present in this series, but in the preceding year a determination was made of the starch by the diastase method. At that time there was found to be a close agreement

between the starch as found by difference and as determined by analysis over the latter part of the series, but over the first part of the series the difference was appreciably greater than the amount of starch found.   This latter condition is apparent with regard to the results obtained on the bran and germ.   It is possibly due to a part of the pentosans being of a higher molecular weight than xylan, but no effort has been made to determine clearly upon this point.

With regard to the flour, the starch is in excess of the difference as found.   Several determinations were made on sugars and starches by the method used in determining pentosans, with results as follows:

Commercial corn sugar	.74%
Merck's pure anhydrous dextrose	1.2%
Wheat starch	1.48%

It is probable that the greater part, if not all, of the apparent pentosans found in flour are from some other product.   It is known that certain pentosans are derived from the nucleins of wheat, and since germ is rich in nucleins a part of the pentosans obtained from the germ would naturally be derived from the nucleins. It is possible also that some of the pentoses obtained from bran are derived from the same body.   The amount of dextrin, sugar and starch in the sample of commercial bran examined is less than 30 per cent while the amount of crude fiber and pentosans is 35 per cent.   Neither of these two latter substances serves any great purposes as an article of food.   Their amount in pure bran would be in excess of what is found in this sample of commercial bran and it thus becomes apparent that the greater part of the carbo-hydrates in pure bran is of very little food value.

There is a marked difference in the amount of cane sugar in the germ, the bran and the flour, while reducing sugars are found in none of them, or at least they are not present in quantities greater than a trace.   Dextrins are present to a considerable extent in the flour and also in the germ.   It is quite certain that the amount in flour will vary with the condition of the grain when it was milled.

It is interesting to note that no reducing sugars were found in any of the samples of fully matured wheat, but that there is an appreciable quantity in the very immature grain. There is also a distinct falling off in the amount of sucrose, of dextrose, of pentosans, and in fact of all substances excepting starch as the grain becomes more mature. The amount of amides in the very immature grain is large, as is expected, for this is the form in which nitrogenous bodies are transferred from the stem of the wheat into the grain.

PROXIMATE COMPOSITION OF CERTAIN WHEAT PRODUCTS

	Patent Flour Per cent	Germ Per cent	Bran Per cent
Moisture	12.50	7.80	11.80
Ash	.40	4.70	5.00
Actual Protein	11.23	25.87	14.65
Amides	.15	2.65	.95
Fat	1.38	11.40	3.80
Crude Fiber	.10	1.35	11.30
Pentosans	2.60	4.90	23.73
Dextrins	5.53	7.00	1.85
Dextrose	trace	trace	
Sucrose	.35	14.60	4.60
Starch and undetermined	65.76	19.73	22.32
	100.00	100.00	100.00
Starch found by analysis	68.75	13.72	16.30
Total nitrogen	2.00	5.07	2.76
Amide nitrogen	.03	.53	.19

TABLE SHOWING THE PROXIMATE COMPOSITION OF WHEAT, IN PER CENT OF THE AIR-DRY MATTER, AT THIRTEEN DIFFERENT PERIODS OF THREE DAYS EACH FROM THE SETTING OF THE GRAIN TO PAST RIPENESS, THE WHEAT BEING GATHERED AND DRIED ON THE STRAW

	I Per cent	II Per cent	III Per cent	IV Per cent	V Per cent	VI Per cent
Moisture	6.75	13.50	13.00	13.60	15.00	14.50
Ash	6.83	5.47	3.80	2.84	2.48	2.24
Actual Protein	11.34	15.39	14.36	12.31	11.74	12.25
Amides	10.85	3.30	1.15	.75	.60	.50
Fat	14.64	4.54	3.02	2.49	2.37	2.42
Crude Fiber	9.91	8.90	6.33	4.41	3.71	3.22
Pentosans	12.46	13.09	11.72	10.37	9.20	8.19
Dextrins	6.80	3.84	2.70	2.60	2.14	2.30
Dextrose	1.69	.62	.23	.10	.08	.06
Sucrose	3.12	2.68	2.60	1.78	1.58	1.50
Starch and undetermined	15.61	28.67	41.09	48.75	51.10	52.82
Total nitrogen	4.16	3.36	2.75	2.31	2.18	2.25
Amide nitrogen	2.17	.66	.23	.15	.12	.10

	VII Per cent	VIII Per cent	IX Per cent	X Per cent	XI Per cent	XII Per cent	XIII Per cent
Moisture............	14.65	15.20	15.35	15.20	14.75	14.80	15.00
Ash................	2.12	2 15	2.10	1.94	1.94	2.06	2.07
Actual Protein.......	12.37	12.37	12.08	12.25	12.19	12.08	12.14
Amides........... ..	.50	.40	.40	.40	.40	.40	.35
Fat................	2.36	2.49	2.41	2.40	2.50	2.43	2.57
Crude Fiber..........	2.93	2.93	2.80	2.77	2.69	2.81	2.87
Pentosans........ ...	7.85	7.86	7.53	7.40	7.85	7.38	7.43
Dextrins.............	2.65	2.50	2.72	2.69	1.74	2.46	2.46
Dextrose............	.07	.05	trace	——	——	——	——
Sucrose.............	1.25	1.40	1.34	1.24	1.34	1.46	1.46
Starch and undetermined	53.25	52.65	53.27	53.70	54.60	54.12	53.65
Total Nitrogen.... ...	2.27	2.25	2.20	2.23	2.22	2.20	2.20
Amide Nitrogen......	.10	.08	.08	.08	.08	.08	.07

TESTS TO DETERMINE THE COMMERCIAL VALUE OF WOOD PRESERVATIVES. A PROGRESS REPORT

By Howard F. Weiss

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INTRODUCTION

A list of the various substances that have been used or suggested for preserving timber from decay would embrace many of those known to industrial chemistry. By-products for which no use could be found have generally taken their last stand as possible preservatives of wood. We have had sent to us for tests the condensed fumes of smelters, the waste liquors of pulp plants, the refuse of tanneries, the skimmed milk of creameries, and miscellaneous assortments of compounds under trade names. Many of these have been culled without any test whatever because the claims made for them were manifestly impracticable. Those, however, which appeared meritorious, or about which numerous inquiries from various consumers were received, were admitted to test.

The object of the tests here described is primarily to obtain information on the practical value as wood preservatives of those compounds or chemicals which fall within this latter classification,

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so that intelligent replies might be given to the various inquiries received. Further, it was thought that such an investigation would show clearly the deficiencies of present practice and pave the way for increasing its efficiency, by suggesting lines for original research.

From 40 to 90 per cent, or an average of about 70 per cent, of the total cost of treating wood is in general due to the preservative alone. The most promising field for decreasing the cost, therefore, lies in decreasing the cost of the preservative used. In ordinary treatments with coal-tar creosote it is common practice to inject approximately ten pounds of the oil per cubic foot of wood, although about one-fifth of a pound will prevent fungous growth; in other words, a factor of safety of about fifty applied to the entire volume of wood is used. The safe reduction of this factor offers one of the many interesting problems.

Before undertaking investigations with new compounds, or improved methods of handling the old ones, it was thought best to first collect certain pertinent data which would be of most immediate value and which would broaden the investigator's viewpoint. The tests here described comprise what has been accomplished thus far and should, therefore, be considered simply as preliminary to the more serious problems involved.

PROPERTIES INVESTIGATED

The practical value of a preservative depends very largely upon the conditions under which it is used, and, as these vary considerably, the investigations must necessarily be broad. With this in view, and with a study of the inquiries received as a basis, the following points were studied in these tests:

1. The important chemical and physical properties of the preservative.

2. The effect of the preservative on the strength of the wood treated with it.

3. The ability of the preservative to penetrate and diffuse through wood.

4 The permanency of the preservative after its injection into wood. This involves a study into its volatility and leachability.

5. The combustibility of the wood treated with the preservative.

TABLE I

PIECE NO	SIZE	LATER CUT INTO PIECE NO (MARK)	SIZE
1	1¼"x1¼"x13"	1—1 / 1—2	1¼"x1¼"x3"
2	"	2—1 / 2—2	"
3	"	3—1 / 3—2	"
4	"	4—1 / 4—2	"
5	"	5—1 / 5—2	"
6	"	6—1 / 6—2	"
7	1¼"x2"x13"		
8	"		
9	"		
10			
11	1¼"x1¼"x13"	11—1 / 11—2 / 11—3	1¼"x1¼"x4" / " / "
12	"	12—1 / 12—2 / 12—3	" / " / "
13	"	13—1 / 13—2 / 13—3	" / " / "
14	"	14—1	1¼"x1¼"x6½"
		14—2	"
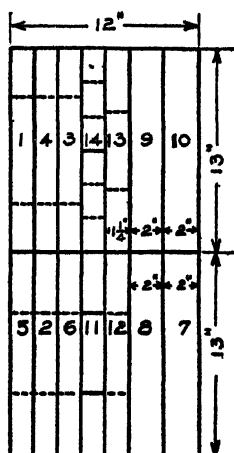
RECUT INTO PIECE NO (MARK)	SIZE
14—1—1	1¼"x1¼"x2"
14—1—2	"
14—1—3	"
14—2—1	"
14—2—2	"
14—2—3	"

FIGURE I

6. The toxic efficiency of the preservative in inhibiting the growth of wood-destroying fungi.

7. The corrosive action of the preservative on steel.

8. The effect of the preservative on paint applied to the wood subsequent to treatment.

Since the investigations were started two other groups of inquiries have become apparent; namely, the effect of the preservative as an *electrolyte* and in *contaminating drinking water*. No systematic tests on either have, however, been made, nor any tests which pertain to a special or limited use.

METHODS OF TEST

The methods by which the various tests were conducted will be only briefly described.

Thoroughly air-seasoned eastern hemlock (*Tsuga canadensis L.*) was selected as the wood best suited for the tests because of its low inherent resistance to attack by fungi, its comparative uniformity of treatment, and its accessibility. Only perfectly clear, straight-grained, and uniform material, free from all mechanical and physical defects, was used; this being cut into test pieces 12″ x 13″ x 1¼″ and recut as shown in Figure 1 and Table 1.

Chemical and Physical Properties of the Preservatives

Under this heading were tested, by standard methods, the chemical composition of the preservative, its specific gravity, viscosity, odor, flash, and burning points. In all distillations the apparatus described in Forest Service Circular 112 was used.

The specific gravity was determined chiefly by a hydrometer or by a Westphal balance. Viscosities were obtained by using the Engler orifice viscosimeter at various temperatures. The flash and burning points were tested by heating the preservative at a rate of 2° C. per minute in an open flash-point tester, passing a small flame over the surface every minute.

Injection of the Preservative

Pieces Nos. 4, 5, 6, 7, 11, 12, 13, and 14-2 were injected with the preservative. Before injection they were oven-dried at 100° C., when they were weighed, and impregnated in the cylinder shown in Figure 2. The simplest procedure (Bethell process) was followed. For example: After the wood was placed in the cylinder the preservative was admitted, displacing the air, until the cylinder was completely filled; a hydrostatic pressure of about 50 pounds per square inch was then applied until the desired absorption was obtained, when the specimens were removed and

weighed within 24 hours; when necessary higher pressures were used.

Strength Tests

Pieces 1, 2, 3, 4, 5, and 6, the latter three treated with the preservative, were tested in bending to failure in an ordinary 30,000-pound testing machine, using a center load over a 12-inch span. Care was taken to have all specimens at approximately the same moisture content at the time of test (about 6 per cent).

Penetrance of the Preservative into Wood

Sticks 4, 5, and 6, after the strength data had been obtained on them, were split and the depth and character of the penetration recorded. This could usually be done visually, but with those preservatives which in aqueous solution were colorless, an aniline dye was used or the specimens were chemically analyzed.[1]

The results from these tests were used to supplement those secured from pieces 8, 9, and 10, which were tested in a specially constructed penetrance apparatus (see Fig. 3) operated as follows: A hole, one inch in diameter, was bored in the center of each stick (E) to a depth of three-fourths inch. The stick was then raised to a temperature of about 180° F. and clamped between two iron discs (F and F¹) so that the preservative could be forced into the hole under a constant pressure and temperature. For oils the length of the pressure period was 30 minutes, and for water-soluble salts, 3 minutes, with the exception of sodium silicate, for which the time was prolonged to 30 minutes. The time it took to penetrate the wood longitudinally was noted, after which the specimen was sawed longitudinally and transversely through the center lines and the penetration radially, tangentially, and longitudinally was studied.

Volatilization Tests

The volatility tests were made on oils only. Within three hours after stick 12 had been impregnated it was recut into three pieces each $1\frac{1}{4}''$ x $1\frac{1}{4}''$ x $4''$ in size, weighed separately, and placed in the

[1] It was found by repeated tests that water and the dye had a tendency to penetrate in some cases slightly farther than the preservative, although the difference was of no practical significance.
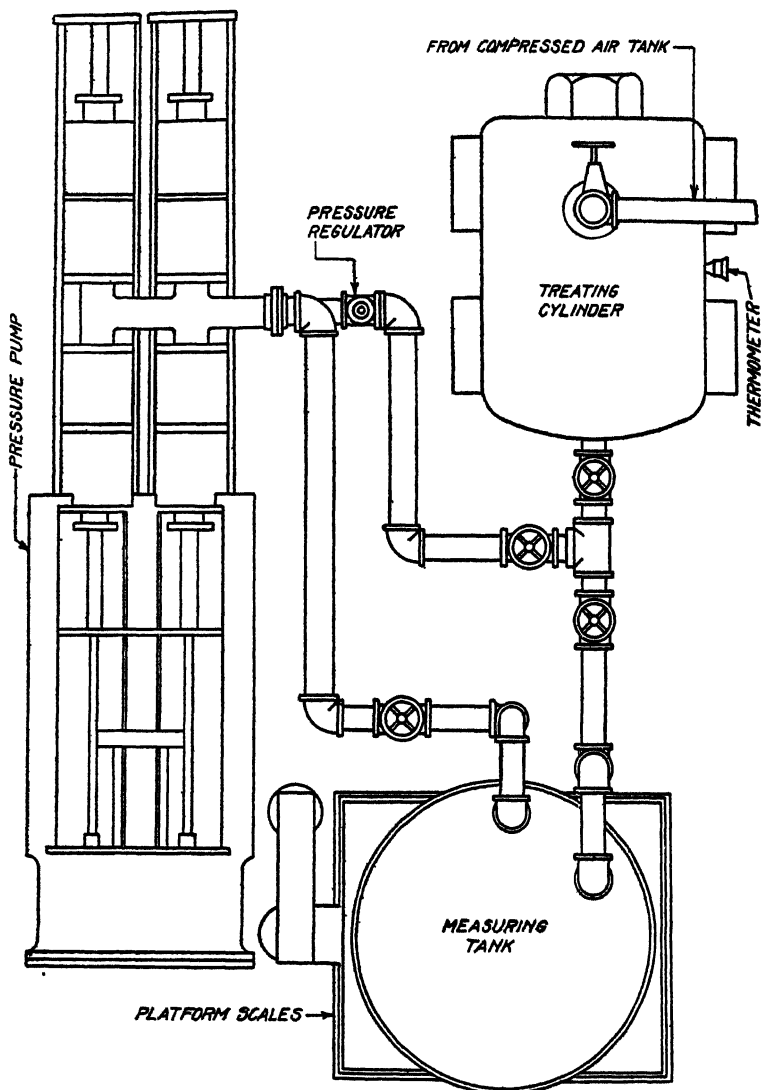
Figure 2. IMPREGNATION APPARATUS

volatility apparatus (see Fig. 4), which consists of an air-tight, metal box, 15″ x 24″ x 30″, through which a constant current of air previously dehydrated by passing through sulphuric acid was passed. The box was heated to 30° C. by electric lamps, the temperature being automatically controlled within 1° C. The treated specimens were removed and weighed at weekly periods for three months. The loss in weight was taken as representing the amount of the preservative volatilized.

Leaching Tests

Leaching tests were made on the water-soluble salts only. Within three hours after stick 13 had been impregnated it was recut into three pieces, each $1\frac{1}{4}$″ x $1\frac{1}{4}$″ x 4″ in size, and weighed separately. Generally, within 48 hours of impregnation these pieces were submerged in a glass jar containing 300 cc. of distilled water at room temperature; this water was changed at stated intervals and analyzed for the presence of preservative. The total time of leaching was four weeks. To check the amount of the preservative remaining in the wood after the total submersion, the specimens were shredded and chemically analyzed.

Inflammability Test

The crib and shaving tests ordinarily used in examining the combustibility of wood were all discarded because of inability to get sufficiently concordant results. This made it necessary to develop original apparatus (see Fig. 5) which consisted of a silica tube, wrapped with nichrome ribbon. An iron tube fitted with a mica sight was cemented below the silica tube.

The specimen of wood, after being lowered in the silica tube, was heated at a uniform rate, by passing twenty-four amperes of electric current through the nichrome ribbon. Temperature readings were obtained from a thermocouple placed beside the specimen and reading direct from a Hoskins pyrometer. A pilot light was used to ignite the gases distilled from the wood. Compressed air partially dehydrated by expansion was passed through the apparatus, its intensity being indicated by a sensitive liquid manometer. Three untreated test specimens were burned as a check against the three treated specimens. When the preservative was
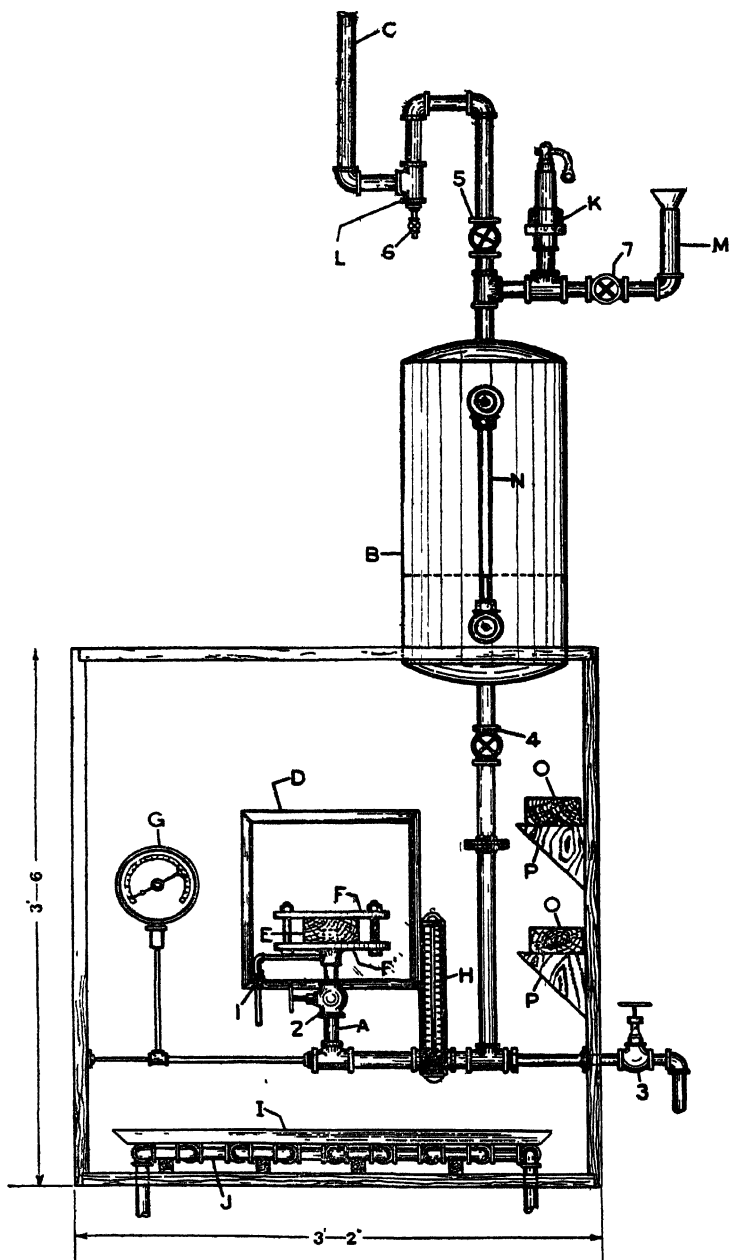
Figure 3. PENETRANCE APPARATUS

a water-soluble salt, the test specimens were first air-dried and then oven-dried before ignition. When the preservative was an oil, one inflammability test was made within twenty-four hours after impregnation and another after three months' seasoning in the volatility apparatus.

Toxicity Tests

Because of the importance of toxicity tests and the inherent objections to various established methods of testing, three methods were followed:

1. Petri-dish method, in which the culture medium was made of juice from one pound of beef, 25 grams Löfflund's malt extract, 20 grams agar-agar, and 1000 cc. of distilled water.

2. The injection of the preservative into wood with a subsequent exposure to an isolated fungus (*Fomes annosus*) Fr. in sterilized jars.

3. The injection of the preservative into wood with subsequent exposure to various fungi in a fungus pit. . Only those fungi which were known to attack wood substance were used.

At present, degrees of decay are determined visually. This method permits of too great error due to the personal equation. To overcome this the extent of attack in these tests was determined by noting the loss in weight of the wood after infection and by forcing a steel ball into it before and after decay, recording the force required to sink the ball to its semi-diameter.

Corrosion Tests

To determine the corrosive action of the preservative on steel a strip of flange steel of the quality specified by the American Society for Testing Materials, August 16, 1909, was submerged in the preservative and heated to a constant temperature of about 98° C. The preservative was changed every week for four weeks in the case of oils; with aqueous solutions it was changed every day for one week. The difference in the weight of the steel before and after submersion was taken to indicate its corrosion. All depositions on the surface of the metal were removed as nearly as possible with a rubber policeman each time the preservative was changed. At the end of the test, where electrolytic deposition of metal had taken place, the deposited metal was removed by acid

TABLE 2.—CHEMICAL AND PHYSICAL PROPERTIES OF THE PRESERVATIVES

Preservative Designated by Co-operator as	Specific Gravity	Degrees C.	Flash point °C.	Burning point °C.	Viscosity (Temperature °C)				Odor	Remarks
					10	50	30	95		
Coal-tar reosote	1.048	60	93	100	3.1	1.7	1.4	1.1	Strong creosote	Graded as "C"
Coal-tar creosote Frac. 1	.934	60	62	69	....	1.1	1.0	.95	Like toluene	Includes oils distilling between 0–205° C.
Coal-tar creosote Frac. 2	1.003	60	79	85	....	....	....	1.0	Strong like naphthalene	Includes oils distilling between 205–250° C. Solid at room temperature
Coal-tar creosote Frac. 3	1.045	60	103	110	2.45	1.4	1.2	1.1	Strong coal-tar creosote	Includes oils distilling between 250–295° C.
Coal-tar creosote Frac. 4	1.088	60	130	136	....	....	1.51	1.11	Mild coal-tar creosote	Includes oils distilling between 295–320° C. Would not flow at 30° C.
Coal-tar creosote Frac. 5	1.150	60	172	178	....	....	80.0	2.6	Mild coal-tar creosote	Includes residue above 320° C.
S.P.F. carbolineum	1.127	16	133	157	....	4.4	2.3	1.25	Tarry (mild)	{ These compounds are similar in many respects. Their exact composition was not determined
Avenarius "	1.126	16.5	139	166	....	7.5	2.4	1.25	Tarry	
C.A. Wood preserver Hardwood tar	1.195	60	90	*	....	17.5**	6.3**	1.4**	Disagreeable pyroligneous	*Water boiled off preventing burning **Viscosity orifice viscometer
Wood creosote (Douglas fir)	1.052	60	45	85	....	15.2	4.9	1.4	Disagreeable pyroligneous	Thi resembled a tar more than a "creosote"
1.07 oil	1.058	60	48	65	16.0	3.7	2.0	1.2	Like kerosene	A water-gas-tar product
Timberasphalt	1.063	60	240	260	....	....	99.2	5.2	Like crude oil	A residuum of petroleum
Copperized oil	.937	25	125	164	....	18.0	5.1	1.5	Like " (mild)	Contains .34% copper
Fuel oil	.87	60	72	101	2.8	1.57	1.3	1.1	Like " (strong)	A crude petroleum

TABLE 2. CHEMICAL AND PHYSICAL PROPERTIES OF THE PRESERVATIVES. *(Continued)*

Preservative Designated by Co-operator as	Specific Gravity	Degrees C	Flash point °C.	Burning point °C.	Viscosity (Temperature °C)				Odor	Remarks
					10	30	50	95		
Zinc chloride	1.028	20	...	...		Same as water			Odorless	Contained 2.67% $ZnCl_2$
Zinc sulphate	1.033	20	...	...		Same as water			Odorless	" 5.9% $ZnSO_4$ $7H_2O$
Zinc sulpha'e by-product)	1.040	20	...	...		Same as water			Odorless	" 6.8% $ZnSO_4$ $7H_2O$
Sapwood antiseptic	1.027	20	...	...		Same as water			Odorless	" 2.92 % $NaCl$ " .246% $CaSO_4$ " .246% $ZnSO_4$ 7 H_2O " .182% $CuSO_4$ 5 H_2O " .06 % $FeSO_4$ 4 H_2O
B. M. Preservative	1.025	20	...	...		Same as water			Odorless	" 0.93% Al. sulphate " 1.8% $ZnCl_2$
Sodium silicate	1.074	20	...	...		Same as water			Odorless	" 8.9% Sodium silicate
Sodium fluoride	1.009	20	...	...		Same as water			Odorless	" 1.2% Sodium fluoride
Cresol calcium	1.075	20	...	...		Same as water			Odorless	2.43% Cresol calcium solution
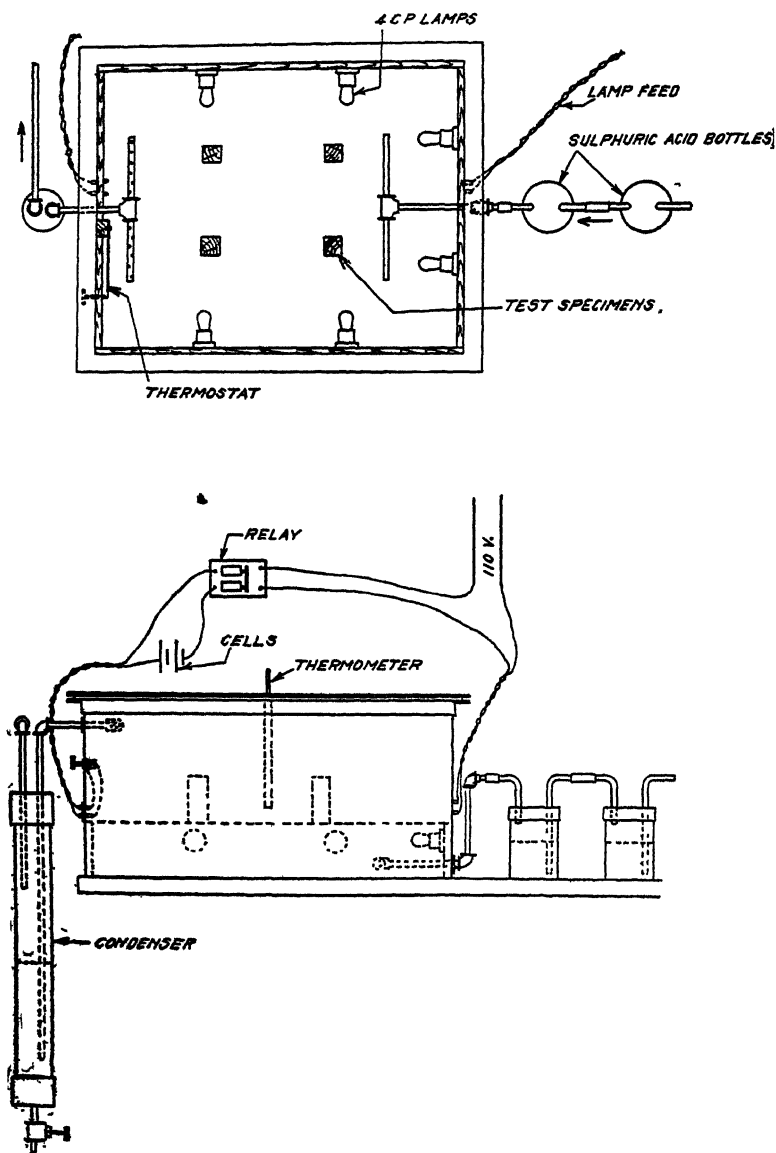
Figure 4.   VOLATILITY APPARATUS

and its amount determined by an analysis of the acid solution. The deposited metal thus obtained was added to the loss of iron and this total represented the total corrosion.

Paint Tests

The treated wood was first air-seasoned for about one month and then coated with white paint (30 pounds of lead oxide to one gallon of linseed oil), noting the color change which subsequently took place.

RESULTS

In the following brief summary of results already secured the author wishes to strongly emphasize that they are tentative only and may be changed in view of subsequent tests, as the field covered is new and errors in manipulation, not at present apparent, might exist. Every feasible precaution, however, was taken to avoid errors and when these were uncontrollable they are so mentioned.

Effect of the Preservative on the Strength of Wood (for details see Table 3)

As a greater accuracy than plus or minus ten per cent could not be obtained in these tests, largely because of variables inherent in wood, the following conclusions should be interpreted liberally:

1. All of the preserving oils, *viz.*, coal-tar creosote, hardwood tar, wood creosote, 1.07 oil, and copperized oil, produced, *per se*, no appreciable weakening in the strength of the wood impregnated with them. The increases in strength noted in some cases were probably due to a lower moisture content in the treated specimens at the time of test. The amount of moisture which they contained could not be definitely determined, although it is believed to be below six per cent.

2. In general, the water-soluble preservatives caused a slight weakening of the seasoned wood. This was most pronounced in the case of sodium silicate and by-product zinc sulphate. The values given for the effect of these preservatives are accentuated, due to the higher moisture content of the treated pieces. The application of a moisture correction factor would probably show that with the exception of sodium silicate and by-product zinc

sulphate the weakening caused by these water-soluble preservatives is of no practical significance.

Penetrance of the Preservative into Wood (for details see Table 3)

TABLE 3.— PENETRANCE OF THE PRESERVATIVES AND THEIR EFFECT ON THE STRENGTH OF WOOD

Preservative designated by co-operator as	Penetration				Average absorption of preservative	Strength in per cent of modulus of rupture of untreated wood	Moisture at Test	
	Rad. and Tang.		Long[1]				Untreated	Treated
	Max.	Min.	Max.	Min.				
	In.	In.	In.	In.	Lbs. per cu. ft.		%	%
Coal-tar creosote	0.28	0.23	6.0	5.3	8.76	93	6.2	....
S.P.F. Carbolineum	0.37	0.23	6.0	5.7+	8.83	...	....	....
Avenarius Ca bolineum	0.17	0.12	6.0	5.3+	8.08	109	6.81	....
Hardwood tar	0.03	0.03	0.92	0.50	6.50	98	6.11	....
Creosote (Douglas fir)	0.08	0.08	3.58	2.33	2.82	107	5.8	....
1.07 oil	0.10	0.10	6.0	3.33	9.58	108	4.52	....
Timberasphalt	0.02	0.02	0.33	0.33	5.68	106	6.68	....
Copperized oil	0.22	0.22	6.0	4.08	8.58	101	5.49	....
Zinc chloride	0.10	0.083	6.0	5.3	0.43a	88	7.13	9.35
Zinc sulphate (by-product)	0.25	0.17	6.0	4.66	1.11b	82	3.88	5.77
Zinc sulphate	0.10	0.08	6.0	4.66	0.96b	89	5.14	9.6
Cresol calcium	0.10	0.10	6.0	3.30	0.46	103	5.72	6.58
B. M. preservative	0.13	0.10	6.0	4.6	0.50b	85	5.16	9.48
Sodium silicate	0.05	0.03	0.46	0.30	0.99	82	6.42	7.38
Sodium fluoride	0.10	0.10	6.0	5.00	0.20	85	5.82	8.7

[1] A penetration of 6 inches was the maximum that could be secured. The absorptions here given have no reference to the data on penetrance.
(a) Dry salt.   (b) For composition, see Table 2.

3. The following preservatives, so far as penetrance is concerned, can be considered satisfactory: Coal-tar creosote; S.P.F. and Avenarius carbolineums, 1.07 oil, copperized oil, zinc chloride, zinc sulphate, cresol calcium, B. M. preservative, and sodium fluoride.

4. The "creosote" from Douglas fir was very difficult to force through hemlock, being about twice as resistant as coal-tar creosote.

5. Satisfactory penetrations with hardwood tar, Timberasphalt, and sodium silicate were not secured. The results indicated that

thcy are from six to eighteen limes as resistant to impregnation as the preservatives mentioned in conclusion (3).

Permanence of the Preservative after Injection into Wood (for details see Table 4)

TABLE 4.—PERMANENCE OF THE PRESERVATIVE AFTER INJECTION INTO WOOD

Preservative designated by co-operator as	Leaching					Volatility					
	Per cent dry salt leached after Immersion in Water for					Per cent volatilized after seasoning for					
	5 days	10 days	15 days	20 days	30 days	10 days	20 days	30 days	50 days	70 days	90 days
Coal-tar[1] creosote	..	..	..	..	..	13	20	24	28	30	32
Coal-ta crcosote Frac. 1[1]	..	..	..	..	..	13	21	26	32	36	..
Coal-tar creo.otc Frac. 2[1]	..	..	..	..	..	8	12	16	20	22	..
Coal-tar crcosote Frac. 3[1]	..	..	..	..	..	7	10	12	15	17	..
Coal-tar creosote Frac. 4[1]	..	..	..	..	..	3	4	4.5	5.0	..	..
Coal-tar creosote Frac. 5[1]	..	..	..	..	..	1.8	2.5	3.0	4.0	..	..
Hardwood tar	..	..	..	..	..	11	12	13	19	20	22
Wood creosote (Douglas fir)	..	..	..	..	..	11	11	17	19	20	28
1.07 oil	..	..	..	..	..	11	8	11	12	14	18
Copperized oil	..	..	..	..	..	1	2	4	6	9	11
Zinc chloride	46	54	57	60	62	..	..	..	..	..	..
Zinc sulphate	42	50	53	56	59	..	..	..	..	..	..
Zinc sulphate (by-product)	47	57	63	65	68	..	..	..	..	..	..
Cresol calcium[2]	21	26	28	31	33	..	..	..	..	..	..
B. M. preservative[3]	43	47	51	54	57	..	..	..	..	..	..

6. After three months' exposure about one-third of the coal-tar creosote injected into the test specimens had volatilized. This was about 4 per cent more than for creosote from Douglas fir, 10 per cent more than for hardwood tar, 14 per cent more than for 1.07 oil, and 21 per cent more than for copperized oil, tested under similar conditions.

[1] The volatility of these fractions are comparable only to each other Their volatilization should not be compared with that of the other preservatives. For absorption of preservative, see Table 3.

[2] Percentage of calcium; cresols not determined.

[3] Percentage of zinc chloride only.

8. The volatility of coal-tar creosote fractions was proportional to their distillation.   Fractions with low ranges, *ceteris paribus*, are less stable than those with high.   At the end of one month the lowest had lost about eight times as much as the highest.

Effect of the Preservative on the Combustibility of Wood (for details see Table 5)

TABLE 5.—INFLAMMABILITY OF TREATED WOOD

Preservative designated by co-operator as	Temerature of Ignition C. Days after Impregnation		Loss in weight due to burning calculated in % of weight before ignition Days seasoned		Character of Combustion
	2	90	2	90	
Untreated wood	320	....	29	..	Burned freely
Coal-tar creosote	173	216	40	27	Burned freely, black smoke, easily extinguished
S.P.F. carbolineum	243	....	26	..	Burned like coal-tar creosote but not so freely
Avenarius carbo-lineum	213	....	32	..	Burned like coal-tar creosote but not so freely
Hardwood tar	190	241	29	30	Burned freely, dense black smoke
W o o d creosote (Douglas fir)	167	217	36	26	Burned like coal-tar creosote
1.07 oil	231	243	40	31	Burned like avenarius carbolineum
Timberasphalt	296	....	28	..	Did not burn freely
Copperized oil	200	228	43	33	Burned like coal-tar creosote
Zind chloride	...	287[1]	..	19	Hard to ignite, burned poorly, easily extinguished
Zinc sulphate	...	304[8]	..	18	Hard to ignite, burned poorly, easily extinguished
Zinc sulphate (by-product)	...	298[1]	..	15	Hard to ignite, burned poorly, easily extinguished
Cresol calcium	...	288[1]	..	29	Burned freely, white smoke hard to extinguish
B. M. preservative	...	305[1]	..	18	More difficult to burn than zinc chloride
Sodium silicate	...	309[1]	..	10	More difficult to burn than B. M. preservative
Sodium fluoride	...	303[1]	..	25	Burned like zinc chloride

[1] Woods treated with salts were ignited as soon as their moisture content was reduced by air seasoning to 6%, usually about two weeks after impregnation. For absorption of preservative, see Table 3.

NOTE.—All salts burned for less than three minutes.   All oils burned for three minutes and were then extinguished.
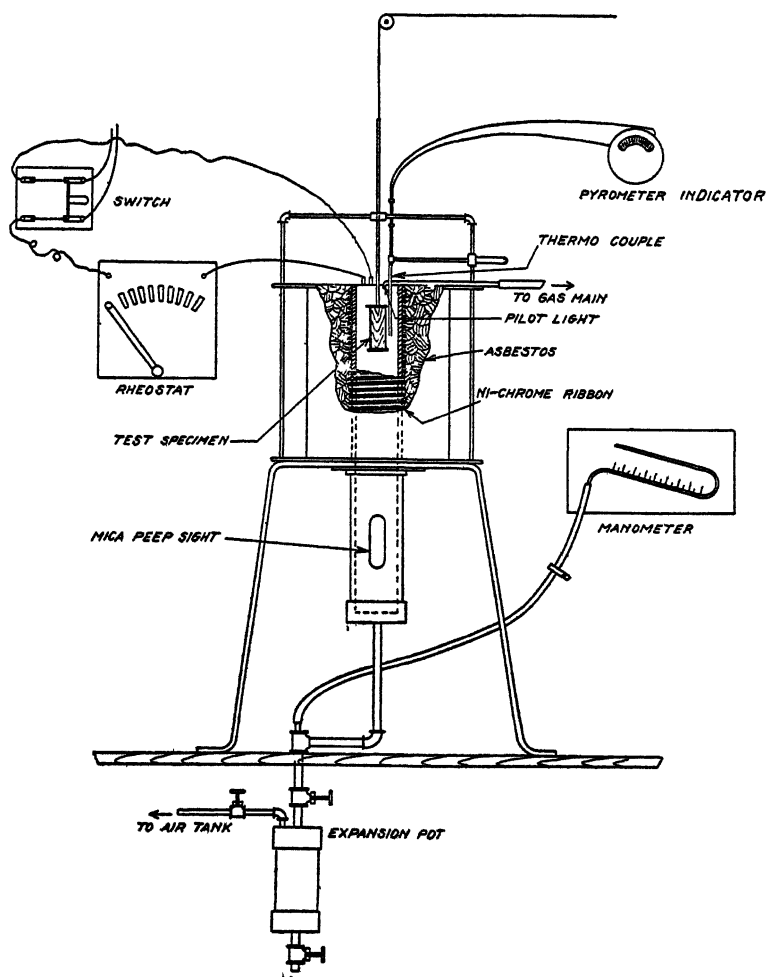
Figure 5.   INFLAMMABILITY APPARATUS

7. After one month's leaching, nearly two-thirds of the zinc chloride injected into the wood had leached.   This loss was 38 per cent greater than the amount of coal-tar creosote which volatilized during the same period.   It should be noted, however, that the test for leaching was much more severe than the test for volatilization.

9. Wood treated with the oils in every case ignited at lower temperatures than untreated wood. When permitted to air-season for three months the temperature of ignition was considerably raised, due probably to the evaporation of the more volatile constituents. The loss in weight from burning treated wood seasoned for three months was also less than in the specimens burned shortly after impregnation (exception — hardwood tar).

TABLE 6.—TOXICITY OF PRESERVATIVES

(As determined by the Petri-dish method against *Fomes Annosus*, Fr.)
0 = no growth.   1 = slight growth.   2 = retarded growth.   3 = strong growth

Per Cent of Preservative	PRESERVATIVES DESIGNATED BY CO-OPERATOR AS															
	Coal-tar Creosote	Coal-tar Creosote Fraction 1	Coal-tar Creosote Fraction 2	Coal-tar Creosote Fraction 3	Coal-tar Creosote Fraction 4	Coal-tar Creosote Fraction 5	S.P.F. Carbolineum	Avenarius Carbolineum	Hardwood Tar	Wood Creosote (Douglas fir)	1.07 Oil	Timberasphalt	Copperised Oil	Fuel Oil	Zinc Chloride	Sapwood Antiseptic
.2	1	2[1]	0	1	1	2	2	2	3	2	3	3	3	3	1	3
.4	0	0	0	0	0	2	1	1	2	....	3	3	3	3	0	3
.6	....	....	....	....	....	2	2	0	0	....	....	3	3	3	....	3
.8	....	....	....	....	....	2	....	....	....	....	3	3	3	3	....	3
1.0	....	....	....	....	....	2	....	....	....	....	3	3	3	3	....	3
2.0	....	....	....	....	....	2	....	....	....	....	3	....	3	....	....	3
3.0	....	....	....	....	....	2	....	....	....	....	3	....	3	....	....	3
4.0	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	3
5.0	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	3[2]

10. In general, wood treated with the water-soluble preservatives ignited at higher temperatures than wood treated with oils, although the temperature of ignition was lower than the untreated wood.[3] Furthermore, wood treated with the water-soluble salts showed in general a less loss in weight after combustion than those treated with the oils. It should be noted, however, that the

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[1] Creosote Fraction 1 is so volatile that concordant results are difficult to obtain. At the close of the experiment it is probable that much of the preservative had evaporated from the medium—which may account for the low toxicity indicated.

[2] Slight growth at 75 per cent.

[3] Wood dipped in a 50 per cent sodium silicate solution ignited at a temperature of 448° C. and its weight was reduced 17 per cent, although it immediately extinguished when dropped in the lower chamber of the inflammability apparatus.

amount of wood actually burned may have been greater than in the case of oils.

11. Untreated wood and wood treated with oils (exception — Timberasphalt) burned freely and in general had to be extinguished after a 3-minute period, while wood treated with water-soluble salts (exception — cresol calcium) burned slowly and became extinguished in less than three minutes.

Toxic Efficiency of the Preservative in Inhibiting Fungous Growth (for details see Table 6)

The following tentative conclusions on the toxicity of the various preservatives may be drawn, although the author wishes to emphasize that they should not as yet be considered final, due to errors peculiar to the Petri-dish method.

12. Zinc chloride and coal-tar creosote offered about the same resistance to the growth of a wood-destroying fungus.

13. The toxicities of the coal-tar creosote fractions distilling below 320° C. were quite similar to each other and to coal-tar creosote.

14. Those portions of coal-tar creosote distilling above 320° C. were but slightly toxic, being at least fifteen times less resistant than the creosote itself.

15. The toxicity of preservatives designated as S.P.F. and Avenarius carbolineums was quite similar, being somewhat less than that for the coal-tar creosote tested.

16. Preservatives designated as 1.07 oil, Timberasphalt, copperized oil, fuel oil, and Sapwood Antiseptic all had no effect in inhibiting fungous growth up to concentrations of at least one per cent.

The methods of determining toxicity by pure-culture-jar and fungus-pit tests have, up to this writing, not progressed sufficiently far to yield definite results.

Although too few determinations have been made to date to draw final conclusions, nevertheless those which have been made indicate that the ball test should prove highly valuable in determining mechanically the extent of decay in wood.

Corrosive Action of the Preservative on Flange Steel (for details see Table 7)

17. Of the various preservatives tested, coal-tar creosote and copperized oil had the least deleterious effect on steel and their action in practical operations can very probably be neglected.

TABLE 7.—CORROSIVE ACTION OF THE PRESERVATIVE

PRESERVATIVE DESIGNATED BY CO-OPERATOR AS	LOSS IN WEIGHT (GRAMS) OF FLANGE STEEL AFTER IMMERSION IN PRESERVATIVE AT 98°C. FOR	
	3 Weeks	4 Weeks
Coal-tar creosote	.0064	. . . . . .
Coal-tar creosote Frac. 1	.0000	.0008
Coal-tar creosote Frac. 2	.0389	.0401
Coal-tar creosote Frac. 3	.0063	.0467
Coal-tar creosote Frac. 4	.0313	.0296
Coal-tar creosote Frac. 5	.0005	.0015
Avenarius carbolineum	.0807	.0951
Hardwood tar	8.2629	11.2350
Wood creosote (Douglas fir)	5.0989	. . . . . .
Spirittine	1.2938	1.5029
1.07 oil	.0243	. . . .
Timberasphalt	.2222	. . . . .
Copperized oil	.0096	. . . . . .
Fuel oil	.0012	.0062
Zinc chloride	1.4636	. . . .
Zinc sulphate (a)	.6050	. . . .
Zinc sulphate (b) by-product	1.3809	. . . .
B. M. preservative	3.1660	4.1746
Sodium fluoride	.1256	.1588
Cresol calcium	.0139	.0181

(a) Equivalent to 2.1% zinc chloride solution.
(b) Equivalent to 6.2% zinc chloride solution.
For concentration of salt solutions used, see Table 2.

18. All the metallic salts were much more pronounced in their action than coal-tar creosote, so that the depreciation in plants using them would, unless precautionary measures were taken, be greater.

19. The very marked corrosion of hardwood tar and creosote from Douglas fir is probably due to the comparatively large amount of acetic acid which they contain.

Discoloration of Painted Wood (for details see Table 8)

20. All the oils tested rendered the wood unfit for subsequent painting. Copperized oil was least objectionable in this respect.

If thoroughly dried after treatment so that excess oil would not appear on the surface, it is possible that wood treated with some of these preservatives could be satisfactorily painted with dark pigments.

TABLE 8.—DISCOLORATION OF PAINTED WOOD

PRESERVATIVE DESIGNATED BY CO-OPERATOR AS	CONDITION OF PAINTED SURFACE AFTER EXPOSURE FOR ONE MONTH
Coal-tar creosote	Very badly discolored and paint not dry
Hardwood tar	Very badly discolored and paint not dry
Wood creosote (Douglas fir)	Very badly discolored and paint not dry
1.07 oil	Very badly discolored and paint not dry
Copperized oil	Discolored, paint somewhat sticky
Zinc chloride	Appearance similar to the untreated specimen
Zinc sulphate (by-product)	Appearance similar to the untreated specimen
Zinc sulphate	Appearance similar to the untreated specimen
B. M. Preservative	Appearance similar to the untreated specimen
Sodium fluoride	Appearance similar to the untreated specimen

21. The water-soluble salts were all satisfactory in that they caused no discoloration of the painted surface. If used under conditions where the wood is subjected to moist air, none of these preservatives might prove commercially satisfactory.

CONCLUSIONS

The depth to which oils can be impregnated varies as some inverse function of the viscosity. As temperature strongly influences the viscosity of oils, and as the diffusion of the preservative through the wood is one of the most important factors in proper treatment, it is concluded that to secure best results both the wood and the preservative should be heated to the proper temperature during the pressure period. Because of the low thermal conductivity of wood, the treatments should not be made too rapidly. With water-soluble salts these precautions are not important.

With coal-tar creosote it appears that the fractions of greatest stability are the least toxic   Present practice rather favors the retention in treated wood of the more volatile fractions by an admixture of the more stable ones. If the toxic values here given are correct, there is in practice being forced into wood about two

and one-half times as much zinc chloride and fifty times as much coal-tar creosote as is necessary to prevent decay.   It is concluded therefore, that more economic results against decay, especially when it is accompanied by mechanical deterioration, can be secured by diffusing the preservative more thoroughly through the wood than by saturating the outer fibres and attempting to retain in the wood the volatile constituents through admixtures of nonvolatile constituents.

In general, the flash or burning point of an oil affects the inflammability of wood treated with it.   Of greater importance, however, is the length of time the treated wood has seasoned, as a prolonged seasoning of such wood raises considerably its ignition temperature. It is concluded that it would be good practice to first season such treated timber before placing it in positions subject to fire.   While wood treated with the water-soluble salts mentioned in these tests was in general less difficult to ignite than untreated wood, nevertheless the presence of such preservatives almost invariably renders the wood slow burning and easily extinguishable.

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SECTION VIb: FERMENTATION.

CONTENTS.

ON RED YEASTS

By Kazuo Ando

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It has been recognized by several investigators that red yeasts are characterized by causing no fermentation and forming no spore. The writer once investigated the atmosphere of a Sake brewery at Nada, Japan, and obtained many red colonies on Koji-gelatin media. Similar red colonies were likewise obtained from one of the twenty-four samples of moto (initial wort, in which the sake yeasts are cultivated chiefly), from which he was attempting to separate the sake yeast. Unfortunately these red yeasts died on keeping during the summer. Afterwards very similar red colonies were obtained from the atmosphere of the fermentation laboratory of Engineering College, Tokio, and upon investigation two distinct kinds of red yeasts were separated from these colonies.

General Observation

At the beginning these red colonies appear, on nutritive gelatin, as a light rose colored, lustrous, round spots, the one kind developing into flat, irregular forms, and the other keeping the round form which is higher at the centre. In both kinds the color becomes deeper as the colonies develop.

When these yeasts are cultivated in Koji-extract, they form at first the so-called yeast-ring on the top, which develops towards the centre along the surface, until at last it covers the surface closely with a red film. This film gradually produces wrinkles and at the same time begins to settle as a red precipitate, which at last fills about one-third of the nutritive liquid. There is, however, a remarkable difference between the films of the two kinds of yeast A and B. The wrinkles of A are thin, easily broken and render the liquid turbid when shaken; while those of B are thicker, broken into comparatively large flakes when shaken and produce no turbidity.

This difference becomes more distinct when Hayduck's solution is used instead of Koji-extract, the yeast-ring of B showing a remarkable appearance in that case. (Phot. No. 1.) The developments on the agar-agar gelatin are as follows:

A develops along the planted line projectionally with a comparatively smooth surface and a rose color, which gradually becomes deeper. (Phot. No. 2, A.) If allowed to develop fully the colony covers the whole surface of the medium and produces wrinkles, which at last spread all over the colony, as in phot. No. 3, A.

B develops along the planted line with a comparatively rough surface, having the same color as A, but on allowing to develop fully, the flat colony covers the whole surface of the medium and becomes a smooth, lustrous surface without wrinkles. (Phot. No. 2, B and No. 3, B.)

The above difference becomes still more distinct when large colonies are produced on agar-agar gelatin, as in phot. No. 13-16, which show the colonies after three weeks' culture at about 17° C. In this case A develops with a comparatively smooth surface and a beautiful coral red color, while B does so with a comparatively rough surface and an irregular edge, but with the same color as A. (Phot. No. 13 and No. 14.) When allowed to stand for many weeks the colonies develop over the whole surface, and A produces deep wrinkles, as in phot. No. 15, while B becomes flat and very lustrous, as in phot. No. 16.

FERMENTATIVE POWER AND ACID-PRODUCING POWER

The writer has repeatedly examined the fermentative power of these yeasts according to Lindner's process and found that they have no power of fermenting arabinose, dextrose, galactose, raffinose, seminose, fructose, maltose, sucrose, dextrin, and inuline, but that they grow moderately well in solutions containing these substances.

The influences of common salt, ethyl alcohol, and acetic acid on the development of the yeasts were examined by adding these substances to Hayduck's solution. The influence of common salt was not shown up to 4%, but with 5% of it the development

Phot. No 1
10 DAYS IN HAYDUCK'S (SOLUTION 15°C)
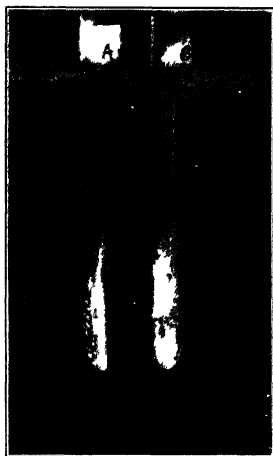
Phot No 2
7 DAYS
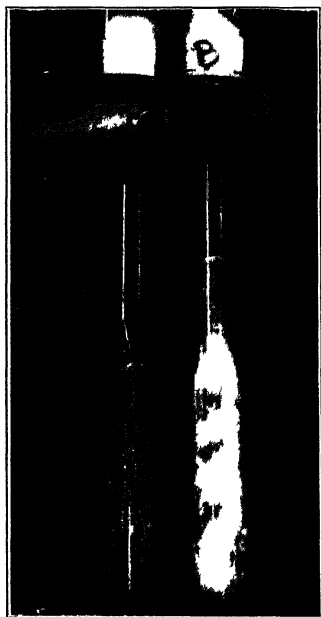
Phot No 3
3 WEEKS (15° C)
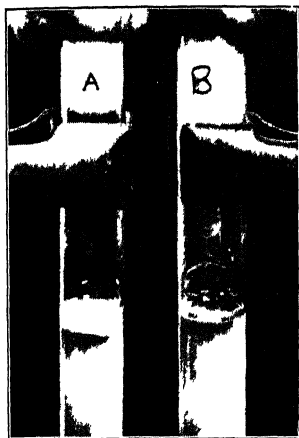
Ihct No 4
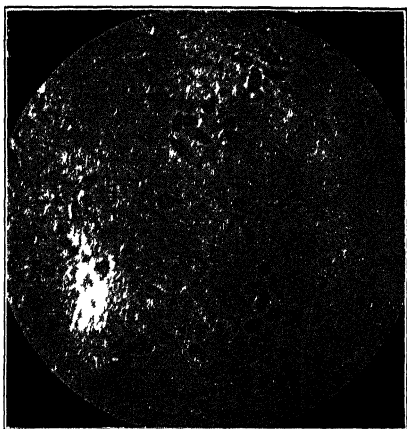
Phot. No 5 (x 660) A
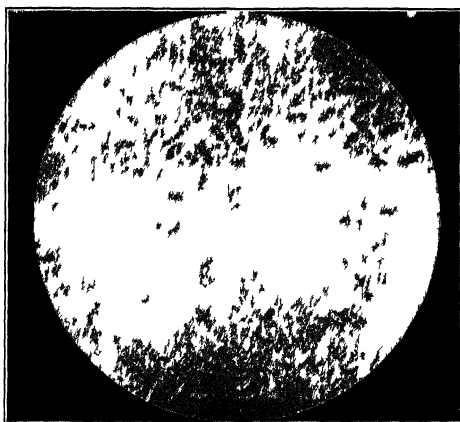
Phot. No. 6 (x 660) B

Phot No 7 (× 660)
A

Phot No 8 (× 660)
B

Phot No. 9 (× 660)
A.
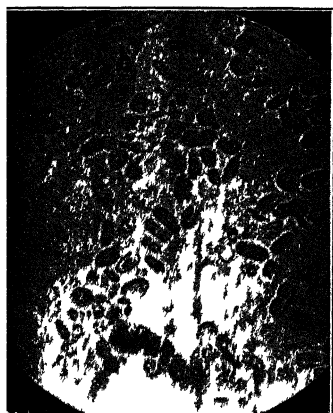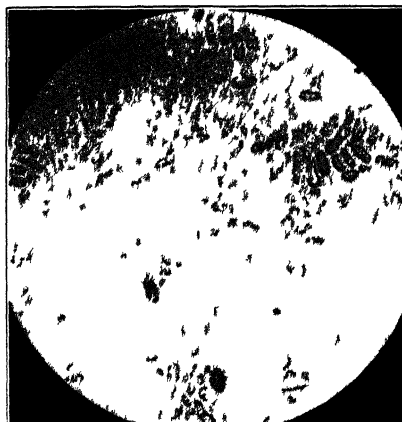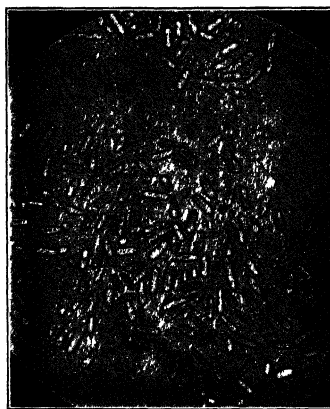
Phot No. 10 (× 660)
B.
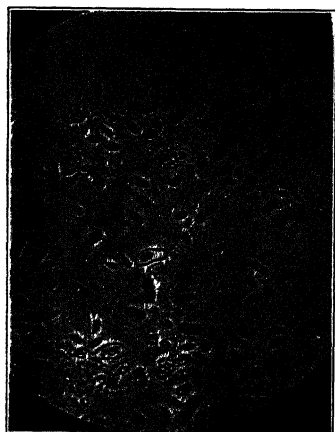
Phot No 11 (× 660)
A GYPSUM CULTURE
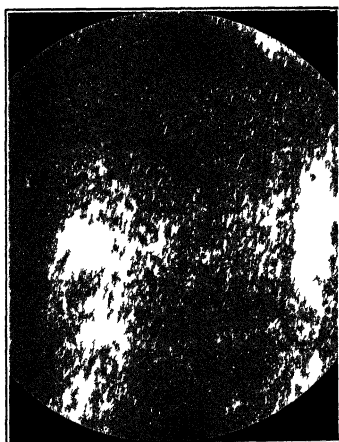
Phot No 12 (× 660)
B GYPSUM CULTURE

Phot No 13
A MODFRATE OLD
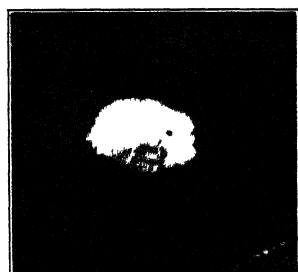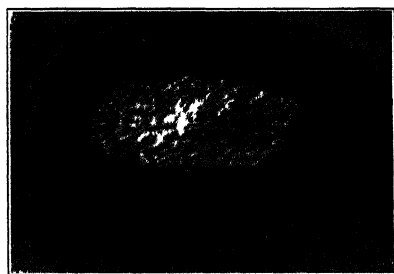
Phot No 14
B MODERATE OLD
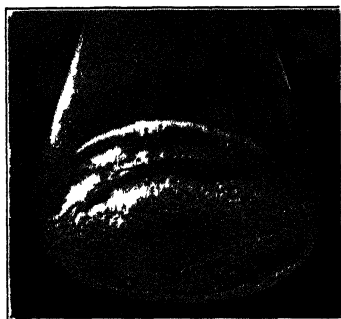
Phot. No. 15
A. OLD

Phot. No. 16
B. OLD

was somewhat prevented, and when 6% was added there was no development whatever. They developed safely in a solution whose alcoholic content was under 6%, but acetic acid was found to have a powerful influence,for when only 0.5% of it was added they did not develop at all.

When the red yeasts were planted in a Hayduck's solution, which contained 5% potato starch instead of cane sugar, there was no growth. When they were planted simultaneously with sake yeast in Hayduck's solution, the sake yeast developed with fermentative action, and the red yeasts, which also developed producing yeast-ring, were found mixed with the sake yeast, which settled down in the later stage. It is evident then that the red yeasts may exist together with sake yeast in the same medium under some conditions.

The acid producing power of the red yeasts was examined by titration with $N_{10}NaOH$, using phenolphthalein as indicator. Each kind of the red yeasts was cultivated in a nutritive solution, 100 c.c. of which consumed 10 c.c. of the alkaline solution, and after the yeasts were fully developed, the solution was filtered and titrated with the alkaline solution. In the case of A, 100 c.c. of the filtered solution consumed 12.86-11.5 c.c. of alkaline solution for total acid, and 12-11 c.c. for non-volatile acid, while in the case of B, 100 c.c. consumed 11.67-10 c.c. for total acid, 10 c.c. for non-volatile acid. These results prove the production of acid by the red yeasts, though in very small amounts.

PRODUCTION OF INVERTASE AND LIQUEFACTION OF GELATIN

The red yeasts were cultured in Hayduck's solution, which was found to reduce a very small amount of Fehling's solution, and after the yeasts were fully developed, the solution was filtered and diluted with water to ten times its original volume. The reducing power of the diluted filtrate was found to be so strong that only 8 c.c. of it sufficed to reduce 100 c.c. of Fehling's solution. No remarkable difference between the reducing power of A and B was observed.

It is evident that temperature has much influence on the liquefaction of gelatin by the yeasts. Both kinds of the red yeasts

were cultured on a 15% gelatin medium at 13 °-15 ° C. for 7 days, when A was found to have partly liquefied the medium, and the developed colonies sank to the bottom of the liquefied portion; on the other hand, B developed over the surface of the medium without liquefying the latter. (Phot. No. 4.) When the temperature was raised to 18 °-20 ° C. B also begun to liquefy the gelatin medium.

MICROSCOPIC OBSERVATION

Young yeasts which are developed in Koji-extract are found to consist of comparatively small, oval cells, and the red color can not be observed even under the microscope. The cells are far smaller than those of true yeasts, such as the sake yeast, the beer yeast, etc. The cells of A are, however, comparatively larger than those of B and among them there are more circular forms. (Phot. No. 5 and No. 6.)

Moderately old yeasts, which have been cultured for a few days, show no remarkable change with B, but in the case of A larger cells are noticeable and also an increase in the number of the circular forms, some of which are beginning to produce tube-formed buds. These differences between A and B become more clearly defined when we compare the fully developed cells. The cells of B then show no change, except that they have shrunk a little; on the other hand, those of A are found to have considerably increased both in their size and in the number of tube-formed buds. (Phot. No. 7-10.)

Sporulation of the yeasts was examined on gypsum, and 1-3 small particles were observed in the cells, as in phot. No. 11 and No. 12. The appearance of these particles, however, differs greatly from that of ordinary spores. That is, these particles reflect the light strongly, and their size is small in comparison with that of the mother cell. The budding power of these cells in the nutritive solution is very weak or none at all, and the small particles remain indifferently at the budding. These particles may consist of either carotine or fat, but are certainly not spores. (Phot. No. 11 and No. 12.)

Coloring Matter of Red Yeasts

There is an idea that the color of microrganisms, such as yeasts, changes according to the nature of the nutritive media and several other circumstances, and that consequently it is not a true characteristic of yeasts. But as for the red yeasts, with which the writer has been experimenting, their beautiful coral red color appears to be a characteristic, at least as much so as the green color is of the plants containing chlorophyl. But, whereas sunlight has generally a great influence upon color in the vegetable kingdom, the color of the red yeasts is developed even in its absence. In fact, the writer has repeatedly compared the culture of the red yeasts on gelatin media in a dark room and in ordinary light, and has found no difference between the two either in color or in the power of liquefying gelatin.

The red color, however, has an intimate relation with the life of yeasts, for if a disinfectant, such as formalin, is added to the colony of yeasts the red color bleaches completely within 24 hours. Hence the red color may be considered as an indication of life.

The red coloring matter of the yeasts is insoluble in water, but moderately soluble in alcohol and more so if hot, producing a rose colored solution. The warm alcoholic solution of the red coloring matter dyes scoured silk a light rose color, which is moderately fast after washing with water. When the alcoholic solution is shaken, with carbon bisulphide, the coloring matter collects in the latter and produces a deep red solution. This solution when kept in a closed tube bleaches in a few days; when it is evaporated upon water bath, the color changes and there is left a solid residue of different nature.

The alcoholic solution keeps its color permanently in a closed tube. It is bleached when an equal or a larger volume of conc. hydrochloric acid or conc. caustic soda solution is added, but acetic acid produces no change.

Conclusion

It may be concluded from the above researches that, although red yeasts exist in the ordinary air and in that of sake brewery,

and would, therefore, appear likely to have some harmful effect upon the brewing industry, they have no direct influence upon it, their existence being limited by the amount of alcohol and acids contained in sake.

These yeasts may be classified under torula, as have been done by other investigators. The utilization of their power of liquefying gelatin and of inverting cane sugar must be made the subjects of future investigation.

ON THE SACCHARIFICATION OF STARCH BY KOJI DIASTASE IN PRESENCE OF ACIDS AND SALTS

BY F. ANDO

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In 1882 Atkinson found in Koji, an enzym soluble in water, invert cane sugar, change maltose, dextrin and starch to glucose (Monit. Scientif. 1882 7). Afterwards O. Kellner, Y. Mori and M. Nagaoka saccharified, with Koji extract, starch and determined the sugars produced (Z. phys. Ch. XIV 297). Moreover, Busgen (Ber. d. d. Bot. Ges. III S. LXVI 1885), Wroblewski (Chem. Ber. 1132 1898), Stone and Wright (Jour. Americ. Chem. Soc. XV 637 Maly's Jb. 1899 720) and J. Takamine (Maly's Jb. 1899 721) investigated about Koji diastase. In 1894 J. Okunura investigated the action of Koji diastase on starch in presence of acids and alkalies, and in 1895 H. Sato studied the saccharification of starch by Koji diastase in presence of fatty acids and salts.

The author investigated the action of Koji diastase on starch in presence of ethyl alcohol (Jour. Brew. Soc. Tokio, 1909 October vol. IV IV-10) and found that the saccharification goes on even in 70% alcoholic solution, contrary to the generally accepted statement that the saccharification stops when the alcoholic content rises to 20 or 30 %.

The Koji diastase used in the experiments was prepared pure by the author from Koji (the mycelium of Aspergillus Oryzae grown on the surface of steamed rice). In order to determine the saccharifying power of the Koji diastase on pure starch solution, which is necessary for control, the following experiment was carried out at the outset.

2 gr. of pure potato starch was put into flasks of about 150 cc each. 30 cc of cold distilled water was added to each of them, well stirred, and after addition of 70 cc of boiling water to each of them the flasks were placed in boiling water bath for 30 minutes,

until the starch was thoroughly jellified. The flasks were then cooled to 50° C. in the air, next transferred to water bath at 50° C. and then 10 cc of 0.1% solution of the Koji diastase was added to each of them. They were stirred during the first hour from time to time, then boiled, speedily cooled, made alkaline with sodium hydroxide solution, diluted to 200 cc and filtered. 25 cc of the filtrate of each flask was taken out, the sugar determined as glucose according to Allihn's method and the percentage contents were calculated, the results being as follows:—

	(a)	(b)
Experiment I	31 9600	31 8800
" II	31 2600	31 6800
" III	30 6800	30 6400
" IV	32.2320	31 9200
" V	31 6600	31 0560

The experiments were carried on twice a day during 5 days, to make the saccharification secure, but the results were found to be nearly equal in all cases.

The experiments in presence of acids and salts were carried on as follows:—

To each flask, 2 gr. of potato starch were added and part of the 30 cc of the distilled water used was replaced with 5% solutions of the acids or salts and after addition of 70 cc boiling water, the flasks were placed in boiling water bath during 30 minutes, cooled to 50° C, 10 cc of 0.1% solution of the Koji diastase added, saccharification continued for one hour etc., as before. As regards volatile acids, they were added when the jellifying was complete, and the further operations were conducted with reverter cooler.

	Volumes of 5% solution of		Per cent. of the compounds
Flasks	Acids or Salts added, cc.	Water, cc.	for Total Volume
A	2.0	28.0	0.10
B	4.0	26.0	0.20
C	6.0	24.0	0.30
D	8.0	22.0	0.40
E	10.0	20.0	0.50
F	12.0	18.0	0.60
G	14.0	16.0	0.70
H	16.0	14.0	0.80
I	18.0	12.0	0.90
J	20.0	10.0	1.00

As above mentioned, each compound was added to 10 flasks in concentrations of from 0.1% and for each 5 flasks (A to E or H to J) were analysed at the same time.

EXPERIMENT I.   Magnesium sulphate

Flasks	Magnesium Sulphate %	(a)	(b)	Average
A	0.10	40.4800	40.3200	40.4000
B	0.20	40.1200	40.1600	40.1400
C	0.30	40.0800	40.2400	40.1600
D	0.40	39.6800	39.9520	39.8160
E	0.50	39.7600	39.9040	39.8320
F	0.60	39.6800	39.7200	39.7000
G	0.70	39.5200	39.5600	39.5400
H	0.80	39.5120	39.0000	39.2560
I	0.90	39.1680	39.0800	39.1240
J	1.00	38.9600	39.0400	39.0000

EXPERIMENT II.   Sodium chloride

Flasks	Sodium Chloride %	(a)	(b)	Average
A	0.10	38.5200	38.0800	38.3000
B	0.20	38.4240	37.9600	38.1920
C	0.30	38.2800	37.5600	37.9200
D	0.40	38.1000	37.0800	37.5900
E	0.50	37.8800	37.0400	37.4600
F	0.60	37.8400	36.8860	37.3630
G	0.70	37.8000	36.8800	37.3400
H	0.80	37.6320	36.8400	37.1760
I	0.90	37.0400	36.8000	36.9200
J	1.00	36.7800	36.4400	36.6100

EXPERIMENT IV.   Potassium phosphate

Flasks	Potassium Phosphate %	(a)	(b)	Average
A	0.10	37.8000	37.8000	37.8000
B	0.20	37.6400	37.6400	37.6400
C	0.30	37.0400	37.7000	37.1700
D	0.40	36.7200	37.1000	36.9100
E	0.50	36.6000	36.8800	36.7400
F	0.60	36.5200	36.8200	36.6700
G	0.70	36.3920	36.4160	36.4040
H	0.80	36.0400	36.1920	36.1160
I	0.90	35.6000	35.9000	35.7500
J	1.00	35.5200	35.7600	35.6400

EXPERIMENT IV.   Acid potassium phosphate

Flasks	Acid K. Phosphate %	(a)	(b)	Average
A	0.10	39.0400	39.3800	39.2100
B	0.20	37.6320	37.6360	37.5340
C	0.30	36.8800	36.5640	36.7220
D	0.40	36.4400	36.5000	36.4700
E	0.50	35.3520	35.7760	35.5640
F	0.60	34.8200	34.9100	34.8650
G	0.70	33.3600	33.7200	33.5400
H	0.80	33.2720	33.4960	33.3840
I	0.90	31.1920	31.3160	31.2540
J	1.00	29.8400	29.6000	29.7200

EXPERIMENT V.   Sodium phosphate

Flasks	Sodium Phosphate %	(a)	(b)	Average
A	0.10	25.7800	25.4800	25.6300
B	0.20	20.4000	20.4000	20.4000
C	0.30	16.5800	16.4400	16.5100
D	0.40	13.4300	13.5200	13.4750
E	0.50	12.7700	12.7000	12.7350
F	0.60	10.7600	10.6000	10.6800
G	0.70	8.8800	8.9600	8.9200
H	0.80	8.2800	8.2800	8.2800
I	0.90	7.3400	7.3200	7.3300
J	1.00	7.1800	7.2000	7.1900

EXPERIMENT VI.   Acid sodium phosphate

Flasks	Acid Sodium Phosphate %	(a)	(b)	Average
A	0.10	39.3800	39.7200	39.5500
B	0.20	37.6360	37.4320	37.5340
C	0.30	36.5640	36.8800	36.7220
D	0.40	36.5000	36.5600	36.5300
E	0.50	35.7760	35.3520	35.5640
F	0.60	34.9100	34.8200	34.8650
G	0.70	33.7200	33.3600	33.5400
H	0.80	33.4960	33.2700	33.3830
I	0.90	31.3160	31.4400	31.3780
J	1.00	29.6000	29.8400	29.7200

EXPERIMENT VII.   Potassium chloride

Flasks	Potassium Chloride %	(a)	(b)	Average
A	0.10	38.4720	38.6000	38.5360
B	0.20	38.3280	38.4240	38.3760
C	0.30	38.2000	38.2800	38.2400
D	0.40	38.1200	38.1600	38.1400
E	0.50	37.9600	38.0400	38.0000
F	0.60	37.9200	37.9200	37.9200
G	0.70	37.8800	37.7600	37.8200
H	0.80	37.6800	37.6000	37.6400
I	0.90	37.6000	37.3360	37.4680
J	1.00	37.0400	37.0800	37.0600

EXPERIMENT VIII.   Potassium sulphate

Flasks	Potassium Sulphate %	(a)	(b)	Average
A	0.10	38.4240	38.5200	38.4720
B	0.20	38.2800	38.7760	38.3280
·C	0.30	38.1200	38.2000	38.1600
D	0.40	37.9400	38.0400	37.9900
E	0.50	37.8400	37.7600	37.8000
F	0.60	37.6400	37.5200	37.5800
G	0.70	37.3360	37.2880	37.3120
H	0.80	37 0800	37.0400	37.0600
I	0.90	36.8400	36.8400	36.8400
J	1.00	36.6400	36.7200	36.6800

EXPERIMENT IX.   Sodium sulphate

Flasks	Sodium Sulphate %	(a)	(b)	Average
A	0.10	39.5200	39.4000	39.4600
B	0.20	38.9200	38.6000	38.7600
C	0.30	38.2400	38.1600	38.2000
D	0.40	38.1200	38.0000	38.0600
E	0.50	37.8000	37.6800	37.7400
F	0.60	37.6800	37.4230	37.5560
G	0.70	37.2880	37.2400	37.2640
H	0.80	37.1600	37.0800	37.1200
I	0.90	37.1200	37.0000	37.0600
J	1.00	36.8400	36.8800	36.8800

EXPERIMENT X.   Potassium carbonate

This compound apparently inhibits the liquifying as well as the saccharifying power of the Koji diastase, thus the contents of the flasks were very difficult to filter even when diluted to 200 cc. The filtrates obtained did not precipitate cuprous oxide perceptibly with Felhing's solution, so the experiments were stopped. A few other compounds showed the same results.

EXPERIMENT XI.   Sodium carbonate

The results were the same as that of the former.

EXPERIMENT XII.   Acid calcium phosphate

The results were the same as that of the former.

EXPERIMENT XIII.   Potassium bicarbonate

Flasks	Potassium Bicarbonate %	(a)	(b)	Average
A	0.10	14.8800	14.0000	14.4400
B	0.20	10.8400	10.1200	10.4800
C	0.30	7.8800	8.0000	7.9600
D	0.40	7.7200	7.7600	7.7400
E	0.50	7.6000	7.6800	7.6400
F	0.60	7.4000	7.4000	7.4000
G	0.70	7.2400	7.2800	7.2600
H	0.80	7.0000	7.0800	7.0400
I	0.90	6.8000	6.7200	6.7600
J	1.00	6.7200	6.6800	6.7000

EXPERIMENT XIV.   Sodium bicarbonate.

Flasks	Potassium Bicarbonate %	(a)	(b)	Average
A	0.10	7.7200	7.8400	7.7800
B	0.20	5.7600	6.5600	6.1600
C	0.30	5.7200	5.8400	5.7800
D	0.40	4.9200	5.2400	5.0800
E	0.50	4.7600	5.0000	4.8800
F	0.60	4.5600	4.8400	4.7000
G	0.70	4.5200	4.5600	4.5400
H	0.80	4.0400	4.1200	4.0800
I	0.90	3.8000	3.8800	3.8400
J	1.00	3.6400	3.6800	3.6600

EXPERIMENT XV.   Ammonium phosphate

Flasks	Am. Phosphate %	(a)	(b)	Average
A	0.10	32.0000	32.0400	32.0200
B	0.20	31.6400	31.6800	31.6600
C	0.30	31.5600	31.4800	31.5200
D	0.40	30.9200	31.0000	30.9600
E	·0.50	30.3600	30.3200	30.3400
F	0.60	29.8000	29.6800	29.7400
G	0.70	29.4400	29.4800	29.4600
H	0.80	28.9200	28.8000	28.8600
I	0.90	28.6400	28.6000	28.6200
J	1.00	28.1200	28.2000	28.1600

EXPERIMENT XVI.   Potassium ioxide

Flasks	Potassium Ioxide %	(a)	(b)	Average
A	0.10	40.1600	39.8560	40.0080
B	0.20	40.0800	39.7520	39.9160
C	0.30	40.0000	39.6000	39.8000
D	0.40	39.9040	39.4800	39.6920
E	0.50	39.6400	39.4000	39.5200
F	0.60	39.4800	39.3120	39.3960
G	0.70	39.4000	39.2160	39.3080
H	0.80	39.2160	39.1200	39.1680
I	0.90	39.1200	39.0000	39.0600
J	1.00	39.0800	38.9200	39.0000

EXPERIMENT XVII. Potassium bromide

Flasks	Potassium Bromide %	(a)	(b)	Average
A	0.10	38.7200	38.7600	38.7400
B	0.20	38.6800	38.5200	38.6000
C	0.30	38.6000	38.2000	38.4000
D	0.40	38.4240	38.0000	38.2120
E	0.50	38.1600	37.7600	37.9600
F	0.60	37.8000	37.5200	37.6600
G	0.70	37.6860	37.3360	37.5080
H	0.80	37.3360	37.2000	37.2680
I	0.90	37.2000	37.0400	37.1200
J	1.00	37.1200	36.8400	36.9800

EXPERIMENT XVIII. Manganese sulphate

Flasks	Manganese Sulphate %	(a)	(b)	Average
A	0.10	38.1700	38.2000	38.1850
B	0.20	38.3760	38.4240	38.4000
C	0.30	38.7200	38.6000	38.6600
D	0.40	38.8800	38.8000	38.8400
E	0.50	39.6800	39.5200	39.6000
F	0.60	39.7200	39 9040	39.8120
G	0.70	41.6400	42.4800	42.0600
H	0.80	42.3200	42.7680	42.5440
I	0.90	43.2000	43.1600	43.1800
J	1.00	44.4800	43.7600	44.1200

EXPERIMENT XIX. Manganese chloride

Flasks	Manganese Chloride %	(a)	(b)	Average
A	0.10	36.1600	36.8000	36.4800
B	0.20	38.8000	39.4000	39.1000
C	0.30	39.6000	39.5600	39.5800
D	0.40	39.9040	39.9500	39.9270
E	0.50	40 '000	41.2880	40.8440
F	0.60	41.7600	41.6400	41.7000
G	0.70	42.1600	41.9760	42.0680
H	0.80	43.5040	42.4400	42.9720
I	0.90	43 6000	43.0000	43.3000
J	1.00	43 7200	43.6000	43.6000

EXPERIMENT XX. Hydrochloric acid

Flasks	Hydrochloric Acid %	(a)	(b)	Average
A	0.10	37.7200	38.2400	37.9800
B	0.20	16.4000	16.7200	16.5600
C	0.30	12.9600	12.6800	12.8200
D	0.40	9.5600	9.6400	9.6000
E	0.50	7.4645	8.4000	7.9323
F	0.60	6.2800	6.4000	6.3400
G	0.70	5.8000	5.9200	5.8600
H	0.80	5.4800	5.4200	5.4500
I	0.90	5.3200	5.3600	5.3400
J	1.00	4.9600	5.1200	5.0400

EXPERIMENT XXI. Sulphuric acid

Flasks	Sulphuric Acid %	(a)	(b)	Average
A	0.10	4.8800	4.9200	4.9000
B	0.20	4.3200	4.3600	4.3600
C	0.30	3.8000	3.7600	3.7800
D	0.40	3.4000	3.4400	3.4200
E	0.50	3.3600	3.3600	3.3600
F	0.60	2.9600	3.0800	3.0200
G	0.70	2.8800	2.9600	2.9200
H	0.80	2.8000	2.8800	2.8400
I	0.90	2.7200	2.7600	2.7400
J	1.00	2.5200	2.4800	2.5000

EXPERIMENT XXII. Nitric acid

Flasks	Nitric Acid %	(a)	(b)	Average
A	0.10	37.5600	37.3360	37.4480
B	0.20	37.0400	36.7600	36.9000
C	0.30	25.2000	25.0000	25.1000
D	0.40	17.4000	17.4800	17.4400
E	0.50	13.8000	13.9600	13.8800
F	0.60	12.1600	12.0000	12.0800
G	0.70	10.0400	10.2000	10.1200
H	0.80	8.3600	8.8400	8.6000
I	0.90	7.2200	7.6000	7.4100
J	1.00	6.7200	6.5600	6.6400

EXPERIMENT XXIII.   Phosphoric acid

Flasks	Phosphoric Acid %	(a)	(b)	Average
A	0.10	14.3200	13 3600	14.3400
B	0.20	8.0000	8.1200	8.0600
C	0.30	7.1200	6.9600	7.0400
D	0.40	5.9200	5.9200	5.9200
E	0.50	4.4000	4.7600	4.5800
F	0.60	4.1200	4.2800	4.2000
G⁻	0.70	3.6000	3.7200	3.6600
H	0.80	3.0000	3.2000	3.1000
I	0.90	2.6800	2.8400	2.7600
J	1.00	2.5200	2.6000	2.5600

EXPERIMENT XXIV.   Acetic acid

Flasks	Acetic Acid %	(a)	(b)	Average
A	0.10	30.8800	30.7200	30.8000
B	0.20	25.8000	25.7600	25.7800
C	0.30	21.3040	21.2080	21.2560
D	0.40	19.1600	18.8800	19.0200
E	0.50	18.0400	18.0000	18.0200
F	0.60	16.0000	15 9600	15.9800
G	0.70	14.8400	14.8000	14 8200
H	0.80	14.5200	14.4200	14.4700
I	0.90	14.4800	14.3200	14.4000
J	1.00	13.8800	13 8400	13.8600

EXPERIMENT XXV.   Lactic acid

Flasks	Lactic Acid %	(a)	(b)	Average
A	0 10	17.1200	17.8400	17.4800
B	0.20	12.8800	12 9200	12.9000
C	0.30	10.3600	11.1600	10.7600
D	0.40	9.6800	9.8000	9.7400
E	0.50	8.7600	8.8800	8.8200
F	0.60	8.7200	8.6800	8.7000
G	0.70	8.3200	8.1200	8.2200
H	0.80	7.6400	7.6800	7.6600
I	0.90	6.6800	6.7200	6 7000
J	1.00	5 5200	5.5600	5.5400

EXPERIMENT XXVI.   Succinic acid

Flasks	Succinic Acid %	(a)	(b)	Average
A	0.10	12.9600	12.7200	12.8400
B	0.20	9.4800	9.2000	9.3400
C	0.30	7.4800	6.2009	7.2000
D	0.40	6.2800	6.2000	6.2400
E	0.50	6.1200	6.1200	6.1200
F	0.60	5.5200	5.4400	5.4800
G	0.70	5.1600	5.2400	5.2000
H	0.80	5.0400	5.1200	5.0800
I	0.90	4.6800	4.6800	4.6800
J	1.00	4.4800	4 5200	4.5000

EXPERIMENT XXVII.   Malic acid

Flasks	Malic Acid %	(a)	(b)	Average
A	0.10	5.9400	6.0000	5.9700
B	0.20	4.6800	4.8400	4.7600
C	0.30	4.6000	4.6800	4.6400
D	0.40	4.4800	4.5600	4.5200
E	0.50	4.2000	4.2800	4.2400
F	0.60	4.1600	4.0400	4.1000
G	0.70	3.9200	3.9600	3.9400
,H	0.80	3 8400	3.8000	3.8200
I	0.90	3.6000	3.7200	3.6600
J	1.00	3.5360	3.4700	3.5040

EXPERIMENT XXVIII.   Tartaric acid

Flasks	Tartaric Acid %	(a)	(b)	Average
A	0.10	4.1600	4.2400	4.2000
B	0.20	3 8800	4.0400	3.9600
C	0.30	3.8400	3.8800	3.8600
D	0.40	3.6000	3 6400	3.6200
E	0.50	3.4400	3.4880	3.4640
F	0.60	3.4000	3.4800	3.4200
G	0.70	3.3200	3.4600	3.3900
H	0.80	3.2800	3.4400	3.3600
I	0.90	3.0800	3.0800	3.0800
J	1.00	3 0000	2.8800	2.9400

EXPERIMENT XXIX.   Citric acid

Flasks	Citric Acid %	(a)	(b)	Average
A	0.10	5.5600	5.2800	5.4200
B	0.20	4.5200	4.7600	4.6400
C	0 30	4.4200	4.6000	4.5100
D	0.40	4.2400	4.2800	4.2600
E	0.50	4.0800	4.1600	4.1200
F	0.60	3.9200	3.8000	3.8600
G	0.70	3.7200	3.6400	3.6800
H	0.80	3.6400	3.5360	3.5880
I	0.90	3.5360	3.4400	3.4880
J	1.00	3.4400	3.2800	3.3600

The foregoing experiments prove that the presence of the acid salts and the neutral salts, with the exception of acid calcium phosphate, is, up to a certain point, favorable to the saccharification. By raising the quantity of the salts added to more than 0.1 gr. the saccharification was gradually retarded; therefore if the quantity of the salts were greatly increased the saccharification would stop; on the contrary, if it were greatly lessened, then the saccharification would be accelerated. Of the salts tried, both neutral and acid, only manganese salts accelerated the saccharification as the quantities increased, apparently resembling the action of sake yeast (Jour. Brew. Soc. Tokio 1910 vol. 10).

The alkaline salts with the exception of potassium phosphate, retarded the saccharification. All acids, whether mineral or organic, retarded the saccharification, except in the samples which contained 0.1 gr. hydrochloric or 0.1-0.2 gr. nitric acids. The facts that in samples containing 0.1 gr. of lactic and succinic acids, the saccharifying power was reduced to about half, and that the action still proceeded even in solutions of 30% alcohol, are very interesting and derserve further investigations.

" UN NOUVEAU PROCÉDÉ INDUSTRIEL DE DISTILLA-TION DU MAIS PAR SACCHARIFICATION ACIDE, AVEC UTILISATION DE TOUS LES SOUS PRODUITS "

Par Emile Barbet

Ancien President de l'association des chimistes de Sucrerie et de Distillerie de France et des Colonies, Paris, France

L'attention des industriels est fixée d'une façon trop exclusive surle rendement en alcool d'un procédé de fabrication Lorsque l'on veut mettre en parallèle les diverses manières dont on peut travailler les grains, il est nécessaire de faire intervenir tous les facteurs qui concourent à produire le bénéfice. En outre il se peut très-bien que tel procédé plus avantageux en France où les grains sont très-chers, devienne inférieur aux autres dans les pays où le grain est bon marché par rapport au prix du charbon. Une troisième considération importante est le coût relatif des installations comme bâtiments et comme matériel mécanique.

Depuis que les procédés de saccharification par le malt vert sont parvenus à obtenir 35 et même 36 litres d'alcool anhydre par 100 Kos de maïs sec, et que l'amylo a atteint 38 et 39 litres, on a pris l'habitude de dédaigner l'ancien procédé de saccharification par l'acide chlorhydrique qui donne péniblement 33 litres. La présente communication a pour but de faire voir qu'il a été possible de modifier les données anciennes de cette industrie, et d'obtenir un si grand nombre de sous-produits sous une forme avantageuse que, dansbein des pays, la balance va pouvoir pencher à nouveau en sa faveur.

L'obtention d'une drèche excellente et bien exempte d'acide avait déjà été réalisée par nous en 1888-89; rappelons-en sommairement le principe.

Le maïs est concassé grossièrement, puis jeté dans des cuves de cuisson préparatoire contenant de l'eau, ou de la vinasse, acidulée

par environ 5 à 6% d'acide chlorhydrique.   Après une cuisson d'environ une heure, le mèlange est envoyé dans une batterie de tamis à la Lespermont, opérant le lavage méthodique de la drèche de maïs pour en extraire toutes les parties solubles, glucose, dextrine, matières extractives, acide, etc.   La drèche parfaitement épuisée et privée d'acide constitue une excellente nourriture; on peut lapresser dans des filtres-presses puisla sécher dans des séchoirs appropriés.

Pendant ce temps le sirop qui s'égoutte des tamis se rend dans une cuve d'attente et de là dans des cuiseurs sous pression, en cuivre (appareils Kruger), cuiseurs dans lesquels, grâce à une pression d'environ 3 kilos, la stransformation de la dextrine en glucose s'achève.

Le sirop est envoyé par la pression du cuiseur dans des cuves où l'on opère la saturation à la craie ou à la chaux. Ce sirop est enfin dilué à densité convenable et mis en fermentation.

Tel était le procédé original; il ne subit aujourd'hui que quelques améliorations de détails:

1°   Les appareils de cuisson préparatoire qui étaient en bois et munis d'agitateurs deviennent cylindro-coniques en cuivre, et n'ont plus besoin de mécanisme, les injecteurs tangentiels de vapeur se chargeant de brasser la masse;

2°   Le débit du tamisage est réglé à l'entrée de la batterie par un robinet à flotteur à hauteur variable; plus le niveau est réglé haut, plusla danaide prélève de liquide à chaque révolution;

3°   Le malaxage de la drèche dans chaque pétrin est amélioré;

4°   La pression de la drèche dans le filtre-presse est donnée par pompe avec un jeu de soupapes de sûreté qui assure une forte compression finale pour bien assécher le tourteau.

La modification la plus importante consiste dans l'augmentation de durée de la cuite préparatoire, qui est portée à 2 h. ½ et même 3 heures suivant la nature des maïs, surcuisson qui rend le tamisage peut-être un peu plus difficile, mais qui donne d'autre part deux avantages énormes:

1°   La solubilisation de l'amidon devient intégrale; et le rendement alcoolique s'élève sensiblement;

2°   Le germe du maïs est complètement désagrégé, et dès lors il passe à travers les mailles de la toile métallique du tamis,

entraînant avec lui la totalité de l'huile du maïs, qui autrefois restait en grande partie dans la drèche des tamis.

Grâce à cette modification la drèche des tamis n'a plus besoin d'être pressée, ni séchée, ni traitée à l'essence pour l'extraction des matières grasses; c'est à peine si la benzine ou l'essence révèlent 1 à 1½ pour cent. de matières grasses, et encore ce n'est pas véritablement de l'huile, mais plutôt une résine de peu de valeur. La drèche, en un mot, peut être donnée telle qu'elle sort des tamis aux bestiaux sans que l'on ait à regretter une perte de matières grasses.

Celles-ci sont un peut dire en totalité contenues dans les fines farines qui sont passées à travers les toiles des tamis. Elles cheminent avec le sirop dans les cuiseurs kruger, puis à la saturation, puis à la fermentation, et enfin à la distillation sans jamais se séparer des cellules de fine farine.

On envoie donc les vinasses dans des filtres-presses; les tourteaux contiennent l'huile. On les sèche et enfin on les traite soit par la presse hydraulique en raison de leur haute teneur en huile, soit par la benzine ou l'essence d'après les procédés usuels. L'huile que l'on récolte est exceptionnellement belle parce qu'elle ne contient pas de résine, celle-ci étant restée dans les drèches. Quel que soit le mode d'extraction choisi, il est d'un emploi facile et économique parce que le tourteau seccontient jusqu' à 36 ou 37% d'huile, richesse véritablement exceptionnelle.

Après l'enlèvement de l'huile, le résidu déshuilé constitue une seconde matière nutritive, laquelle était perdue dans l'ancien procédé.

Enfin la vinasse sortant des filtres-presses étant limpide et contenant très peu d'impuretés, il devient très facile de la concentrer à multiple effet en vue d'en extraire la glycérine de fermentation qui a une si grande valeur commerciale depuis quelques années. Le résidu de cette extraction constitue finalement un engrais organique azoté.

Mais voici une variante de travail qui fournit encore un sous produit de plus:

Après la cuisson sous pression dans les kruger, et après la saturation à la craie, les sirops troubles sont tout de suite envoyés aux filtres-presses, lesquels de préférence sont à lavage des tourteaux.

Les tourteaux obtenus sont délayés dans de la vinasse claire ou dans de l'eau pour retirer le sucre qu'ils contiennent, et passés une seconde fois aux filtres-presses à lavage. Les petits jus qui en résultent sont réunis aux sirops de premier jet, refroidis et envoyés à la fermentation.

Celle-ci ne reçoit donc qu'un liquide absolument clair et même brillant. A la fin de la fermentation on peut récolter par décantation ou par turbinage, puis par le filtre-presse une proportion importante de levure excellente pour fermentations industrielles ou pour d'autres usages.

Il va sans dire que pour rendre économique la concentration des vinasses en vue de l'obtention de la glycérine, on fait rentrer dans le travail de préparation, de tamisage et de lavate des tourteaux la plus grande partie possible de vinasse; une bonne moitié de la vinasse peut-être ainsi réutilisée, de telle façon qu'en fin de compte la glycérine se trouve réunie dans un volume de vinasse deux fois moindre à évaporer.

En résumé, malgré le coût élevé du maïs par rapport aux autres substances alcooligènes, cette substance peut lutter avantageusement et donner de beaux bénéfices par la multitude de produits et sous-produits que le procédé décrit fournit à l'industriel.

Il faut encore ajouter que le rendement en alcool est plus élevé que par l'ancien procédé acide à moût trouble; nous attribuons cette amélioration du rendement au fait que le sirop traité sous pression de 3 kilos est plus dilué; on peut pousser jusqu'à disparition totale de la dextrine sans risquer de caraméliser et de détruire du sucre comme cela se produisait autrefois.

L'augmentation du poids utile des drèches provient de ce que la majeure partie des matiéres extractives du grain n'est plus soumise à la brutalité de l'acide dans l'autoclave, de sorte que la dissolution des matiéres azotées et nutritives est réduite au minimum. On s'en aperçoit très bien à la qualité du flegne obtenu à la colonne distillatoire; ce flegme est d'une finesse très caractéristique et pourrait servir de base à un excellent genièvre ou whisky.

En un mot, alors que la distillation du maïs à l'acide était désignée de la plupart des industriels qui lui préféraient le malt ou l'amylo, cette fabrication rénovée par les améliorations qui

viennent d'être décrites, se présente sous un jour très-favorable et si l'on ajoute en terminant que les dépenses d'installation du matériel sont sensiblement moindres que pour les autres systèmes, on peut en conclure que dans bien des pays l'avantage industriel pourra pencher à nouveau en faveur de la saccharification acide.

SULFUROUS ACID IN WINE–MAKING

By Frederic T. Bioletti

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I. *Introductory and Historical.*

    (a) Controversies over the use of SO_2 in food products.
    (b) Antiquity of the use of SO_2 in wine-making.
    (c) Opinions of enological experts.
    (d) Objects of the use of SO_2.

II. *Forms and Methods of Use.*

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III. *Amounts Necessary.*

    (a) Legal limitations.
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IV. *Effects on Must and Wine.*

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    (d) Extract.
    (e) Acidity.
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    (g) Color.
    (h) Quality.

I. Introductory and Historical

(a) *Controversies over the use of sulfurous acid in food products.*
Recent pure food legislation has very properly attempted to
prevent or restrict the use of antiseptics for the preservation of
substances intended for human consumption.

There are two principal objections to the use of antiseptics for
this purpose. First: Antiseptics are all more or less poisonous
if used as food preservatives. Second: Antiseptics are often,
perhaps usually, used to disguise imperfect material and to
obviate the employment of cleanly and careful methods of prepa-
ration and storage. It is claimed that some antiseptics, notably
Sodium benzoate, if used in certain small proportions, are harm-
less to health. Even if this is correct, the second objection may
apply with equal force.

Most of the opposition to this branch of pure food legislation
comes from those who find profit in the cheap and careless manip-
ulation of inferior products. One who defends or advocates the
use of any antiseptic in the manufacture of any material intended
for consumption, therefore, finds himself in bad company and
liable to suspicion.

The universal and indiscriminating condemnation of all anti-
septics in all cases, however, is liable to work injustice to the inno-
cent and to trammel some of the time-honored methods of food
preparation whose only objects and effects are the improvement
of the quality and wholesomeness of the product. This seems
to have occurred in respect to the use of sulfurous acid in the
manufacture of wine in California and the main object of this
paper is to try to present the subject from the point of view of the
progressive and conscientious wine-maker whose main object is
to present his product to the consumer with those qualities of
agreeableness and healthfulness that alone can give stability to
his market.

To justify the use of sulfurous acid for this purpose it is neces-
sary to show, first: That, as used, it is innocuous and, second:
That the resulting wine is better from the point of view of the
consumer.

The *a priori* argument that all antiseptics are injurious is not valid because not true. Such condiments as pepper, mustard and vinegar, such substances as lactic and citric acid, sugar and alcohol, have antiseptic properties, yet when used in moderate amounts may be harmless or even have a distinct food value. The argument that because a substance is harmful in large amounts it is still harmful though in a less degree in small amounts is still less tenable. The wholesome citric acid of oranges may in a concentrated form cause severe gastric disturbances. The fact that even small quantities of a substance are harmful to certain abnormal or diseased constitutions should also be considered with caution. If we were to consider this a criterion of wholesomeness we should reject sugar, and even many of our best fruits and vegetables.

Many careful tests have been made regarding the effect of small quantities of sulfurous acid on the health. J. Laborde[1] has shown that there was no appreciable effect on the health of either men or dogs after consuming daily for more than a month 1.5 liters of wine containing 500 milligrams of sulfurous acid per liter, 100 milligrams being free. This is more than the most liberal legal limit and several times greater than is needed in the manufacture of most wines.

Perhaps the most convincing though indirect evidence of the harmlessness of sulfurous acid as properly used in wine-making is furnished by the report of Dr. H. W. Wiley[2] on the subject. To twelve young men, sulfurous acid was administered in various amounts for twenty days. The amounts taken varied from .113 to 1.02 grams per day, averaging for the whole period from .213 to .628 grams. This is slightly less than was used in Laborde's experiments where .75 gram was taken.   There was, however, a very marked and important difference in the form of the sulfurous acid. In Laborde's experiments only .15 gram was free or combined with sodium in the form of sulfite. As will be shown later, the effect of free sulfurous acid or the sulfurous acid of sulfites is totally different from that of sulfurous acid combined

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[1]Revue de Viticulture, No. 860, p. 629.

[2]Bulletin No. 84, Part III, Bureau of Chemistry, U. S. Dept. of Agric.
Circular No. 37, Bureau of Chemistry, U. S. Dept. of Agric.

with sugar or aldehydes, the form in which most of it occurs in wine. Its antiseptic effect has been estimated to be only about $\frac{1}{50}$ that of the free. The young men in Dr. Wiley's tests, therefore, received from two to six times as much *effective* sulfurous acid as was ingested by the men in Laborde's tests and from five to forty times as much as they would receive in drinking ordinary wine.

Moreover, it does not seem unreasonable to suppose that in the concentrated form as administered by Dr. Wiley any injurious effects would be intensified.

In spite, however, of these exaggerated doses, the results were slight and uncertain. Some of the young men experienced some uneasiness, while others claimed to feel better[1]. By reference to Table III — pages 799, 800 of Bulletin 84, it may be seen that the six individuals who received sulfurous acid in the concentrated form lost on the average 1.3 per cent. of their weight, while those who received it in a more dilute form gained in weight slightly. A fair deduction from these results would seem to be that even with relatively *large doses* of *free* sulfurous acid in *concentrated* form the effect on the body weight is only slightly unfavorable and that in dilute form it is slightly favorable. Whether this throws any light on the effect of its use in wine in *much smaller* quantities and in a *much less active* form is doubtful. What evidence it does afford tends to show that it would be innocuous.

(b) *Antiquity in the use of sulfurous acid in wine-making.* There is evidence that the use of the fumes of burning sulfur in wine-making was known to the Egyptians and to the Romans. Whether its use was confined to the disinfection of containers or included also the control of the fermentation seems uncertain. That its use for the latter purpose is also of great antiquity is, however, clearly indicated by the fact that it exists in practically all wine-making regions. The enological literature of the 18th century contains numerous favorable references to the beneficial effects of sulfur fumes on the quality of wine.

It is worthy of note that sulfurous acid in this form has been most generally employed in those regions which have long been

[1] Bulletin No 84, Part III, Bureau of Chemistry, pp. 774, 777, 782.

famous for the high quality and wholesomeness of their products, i. e., the Rheingau, Burgundy and the Gironde. It has been least commonly employed in those regions where the quality of the light wines is defective and where the practice of making highly alcoholic wines, fortified with distilled spirits is usual.

The old practice of sulfuring was strictly empirical, based on secular experience and established custom. Its correct employment, therefore, was possible only in a few cases and in the hands of wine-makers of long local standing. In the hands of beginners and in new localities it often failed and even introduced defects into the product. It was not until the beginning of the last decennial of the 19th century that the scientific study of the effects of sulfurous acid on must and wine was seriously undertaken. In 1894 A. Bouffard of Montpellier[1] called attention to the utility of sulfurous acid in controlling the " breaking " or " casse " of wines. Since this date, the investigations of Martinand and Semichon in the south of France, of Laborde in the Medoc, of Pacottet in Burgundy, R. Marès in Algeria and of numerous other enological investigators have succeeded in explaining clearly the main effects of sulfurous acid in the various operations of wine-making. The knowledge thus acquired has made it possible to avoid most of the mistakes made in the use of sulfurous acid by the old wine-makers and to generalize its employment to almost all classes of wine.

(c) *Opinions of enological experts.* That the conclusions of all these investigators are favorable to the proper use of sulfurous acid in wine-making is demonstrated by reference to their latest writings.

In the last edition of Babo u Mach,[2] we read, "Der Schwefel . . . ist entschieden unentbehrlich." " In Kellern . . . in denen die Schwefelschnitten nicht bekannt sind, findet man wohl kaum vollkommen tadellose, handelsfähige Ware." L. Matthieu,[3] speaking for Burgundy, says: " On obtient des vins ayant le maximum de qualité par le méchage préable des moûts."

[1]Comptes rendus de l'Académie des Sciences, 9 Avril 1894.

[2]" Kellerwirtschaft: " Babo u Mack, p. 326, 1910.

[3]" Revue de Viticulture," No. 901, p. 243, 1911.

E. Dupont[1], says as the result of his experiences with sulfurous acid in the south of France: " La diffusion de son emploi à la propriété dans le sens d'une veritable méthode générale de vinification s'impose." And further: " En fait, on est obligé de reconnaître que c'est surtout depuis la vulgarisation de son emploi par le sulfitage des vendanges, que le nombre des vins mal faits, défectueux ou malades, autrefois si frequents,   .   .   . a considerablement diminué; ces vins ont meme à peu très disparu du marché."   .   .   .

J. Laborde[2], discussing the preparation of the white wines of the Gironde states, " Donc, l'addition de l'acide sulfureux dans le vin blanc est un bien, une nécessité même."

Prof. Roger Marés of Algeria in a recent private letter states that since the rational use of sulfurous acid has become general, the inferior, unwholesome wines which were formerly so common in Algeria have practically disappeared and the commercial value of the wines has in many cases been doubled.

Finally, at the last meeting of the *Congrés Internationale de Viticulture* at Madrid in 1911, five resolutions regarding the most important improvements in wine-making were agreed to. Three of these resolutions specify the use of sulfurous acid.

It may be concluded, therefore, with a considerable degree of confidence, that all investigations made with adequate chemical and technical knowledge concur in showing the utility and advisability of the proper use of sulfurous acid in the manufacture and handling of wine.

(d) *Objects of the use of sulfurous acid.* This acid is used universally in wine-cellars for the disinfection and preservation of casks. This was undoubtedly its first use and probably led accidentally to the discovery of its still greater utility in controlling the fermentation of wines.

It is with this latter use, in which the acid is introduced directly into the must or wine, that modern developments and improvements have principally to do. At first, its use was confined almost exclusively to the handling of white wines, under the

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[1] " Revue de Viticulture, No 873, p. 259, 1910.

[2] " Revue de Viticulture," No. 860, p. 624, 1910.

impression that its action was harmful to the color of red wines. This has been shown to be a mistake and now it is regarded as even more essential to the manufacture of wholesome red wines.

In a general way, it may be said that it is used now first: For its *direct* effects on the color and the oxidation of the wine, and second: For its *indirect* effects on the acidity, fixed and volatile, the alcohol, the clearing and aging and on the flavor, odor and conservation, by means of its influence on the various microorganisms and enzymes which occur in must and wine.

II. Forms and Methods of Use

(a) *Sulfur fumes.* The oldest and still the most common source of sulfurous acid is the fumes of burning sulfur. The sulfur is burnt on an earthenware or iron dish at the bottom of a closed cask or, in the case of small casks, on a wick or core of paper, cloth or asbestos suspended by means of an iron wire about half way from the bottom. Wine or must is then pumped into the cask and absorbs SO_2.

This method is defective in many ways.

It is difficult to apply it in the manufacture of red wines, which are nearly always fermented in open vats.

It is impossible in many cases to control the dose applied except within very wide limits. Before fermentation, it is difficult to cause the must to absorb sufficient SO_2 by this means; after fermentation, it is difficult to avoid the over-sulfuring of the wine.

The amount of sulfur which it is possible to burn in a closed space filled with ordinary atmospheric air is limited by the amount of oxygen present. If all the oxygen present in a cask combined with sulfur to form SO_2 the amount formed would correspond to about .046% of the weight of the must which the cask would contain. Tests by W. Cruess[1] show that in small vessels (2600 c. c. flasks) under these conditions only .02% of SO_2 is formed. Babo and Mach[2] state that 400 c. c. of must poured into a 1500 c. c. flask in which all the sulfur possible had

[1]Cruess, W., Zymologist, Agr. Exp. Station, Berkeley, Cal.
[2]Babo and Mach " Kellerwirtschaft," p. 328.

been burnt absorbed .0264% of SO_2 equivalent to .0067% of the total volume of the flask. This shows that less than one half of the amount of SO_2 corresponding to the oxygen in the cask is formed and that the must absorbs only about one third of this amount.

This amount is only about one third of that sometimes necessary in defecating must, and a still smaller part of that used in the fermentation of red wines and the transportation of must. It is, however, from two to five times as much as should be used in the racking and handling of most wines after fermentation.

These results cannot be used in the estimation of the amount of sulfur to burn when the lighter sulfurings are needed. The smaller the amounts of sulfur burnt in a cask of a given size, the greater the proportion of SO_2 formed and the more completely this is absorbed by the must or wine. According to P. Pacottet[1] the amount of SO_2 absorbed varies in various cases from 15% to 60% of the amount corresponding to the sulfur burnt. F. Chabert[2] shows that in some cases it may reach over 90%. With light sulfurings such as are usual in racking wine, if proper precautions are taken, the transformation and absorption may be considered integral and the weight of sulfur used is a sufficient measure of the SO_2 utilized. With heavy sulfurings, such as are necessary in the control of fermentation, it is of very little value for this purpose.

The proportion utilized will be greater in large casks than in small and when the liquid is introduced as a spray from above than when introduced in a solid stream from below. Under average conditions in small casks and with heavy sulfurings, it will be about half of the total amount present or from $7\frac{1}{2}$% to 30% of the theoretical amount corresponding to the amount of oxygen in the air of the cask. This will represent for the heaviest single sulfuring an amount of SO_2 corresponding to from .003% to .014% of the weight of the liquid. The smallest amount is about the maximum for the racking of wine but we have no assurance that larger amounts will not be introduced. The largest amount

[1] Revue de Viticulture, Vol. 26 p. 174.
[2] Progres Agricole et Viticole 1902.

usually is too little for the treatment of must or grapes before fermentation.

The sulfur which is not transformed to SO_2 is either melted, sublimed, or oxidized to sulfuric or other sulfur acids.

The hot melted sulfur, if allowed to fall into the cask, may injure the wood of the staves. The wood thus injured becomes spongy, may decay and is liable to communicate unpleasant flavors to the wine.

The sublimed sulfur is deposited on the walls of the cask and in its finely divided condition is easily reduced by yeast and mycodermae to hydrogen sulfide, mercaptan and other compounds which even in minute quantities communicate disagreeable odors to the wine. According to tests of W. Cruess, small quantities of H_2S may even be formed during the combustion of sulfur in the cask

The sulfuric acid formed will vary according to the conditions of burning, but is said to always exceed 5% of the weight of the sulfur consumed.

The impurities of the sulfur are usually not of consequence, but minute quantities of arsenic may occur, which while insufficient to be poisonous may produce arsenids of persistent garlic odor. Other unfavorable effects on the flavor may originate in the burning of the cloth of sulfur wicks.

With all these defects and uncertainties it is remarkable how successfully experienced wine-makers in the older regions utilize this source of sulfurous acid. In newer regions, with less experienced manufacturers and with new methods of wine-making, the defects are less completely avoidable.

Improvements have been made by burning the sulfur in specially constructed furnaces or sulfur machines which enable the wine-maker to eliminate most of the by-products of the reaction and to control more accurately the amount of SO_2 which he introduces into his must. The defects, however, are not completely eliminated and the devices are more or less troublesome and costly in their operation and suited only for large scale operations.

(b) *Sulfites.* Sulfurous acid is released from its combinations with bases by the action of the acids of the must and wine. Sul-

fites can therefore be used as a source of SO_2. Some sulfites are unstable and variable in composition; some are difficult to handle, measure or obtain pure; others would introduce foreign substances into the wine. Certain potassium salts of sulfurous acid are free from these objections.

The most suitable of these salts is the anhydrosulfite or meta-bisulfite of potassium, $K_2S_2O_5$. This salt is formed by passing gaseous SO_2 into a solution of K_2CO_3 and washing the crystals formed, with concentrated alcohol. It is more stable than the other potassium salts and when pure contains more sulfurous acid — viz. — a little over 57%.

It is easily obtained in commerce free from injurious impurities. Analyses by F. Chabert[1] of samples obtained from reputable dealers showed no impurities except the harmless potassium sulfate. They contained from 52.4% to 54.79% of SO_2. The salt gradually loses strength by the escape or oxidation of the SO_2 but the change is very slow if care is taken to exclude air and moisture. In practice it is usual and sufficient to consider that the salt contains 50% of SO_2.

The potash liberated by the escape of the SO_2 combines with the acid of the wine, forming tartrates which are precipitated. The amount of acidity taken from the wine in this way, however, is very small, and abundantly compensated by the acidity protected from the destructive action of certain micro-organisms always present in the wine.

(c) *Liquified SO_2*. If pure sulfur is treated with sulfuric acid at 400° C gaseous SO_2 is produced. This gas, after washing and cooling to —10° C to free it from water is easily liquified by slight pressure.

The dry, pure liquid produced in this way does not attack metals and has none of the suffocating odor of the fumes of burning sulfur. It has a density of 1.4 at 15°C and boils at —10°C. Its vapor tension is 1.5 atmospheres at 0°C rising only to 6 atmospheres at 40°C. It can therefore be stored and transported in metal containers of comparatively light weight. It is perfectly stable in composition and will neither burn nor support combustion.

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[1]Progrés Agricole et Viticole, No. 3, 1902.

In most respects it is the best form in which SO₂ can be used for all the purposes of the winemaker. Its principal defects are the difficulty of obtaining it in many regions and the necessity of a somewhat expensive measuring appliance.

Solutions of SO₂ in water and alcohol have been used to a limited extent but are so bulky and unstable as to be quite unsuitable.

(d) *Substitutes.* Many substances and methods have been suggested as substitutes for sulfurous acid in winemaking; among them gypsum, phosphates and even salt. None of them accomplish all the objects attained by the use of SO₂ and most of them introduce undesirable substances or qualities.

The method of Rosenstiehl succeeds more nearly than any other. This method consists in the discontinuous or intermittent sterilization of the must in an atmosphere of carbonic acid before fermentation. The method requires very costly apparatus and has therefore never entered into general practice anywhere. There is, moreover, strong reason to doubt whether it will accomplish all the useful ends of sulfuring or be suitable for the manufacture of the more delicate wines of high quality.

III. Amounts Necessary

(a) *Legal limitations.* The recognition of the injurious effects of sulfurous acid in certain cases and a confusion of the effects of the free acid with those of its compounds led to drastic legal limitations on its use.

Switzerland in 1887 restricted the amount allowable in wine to .0008%, the same limitation being adopted in Austria the following year. Bavaria in 1890 increased this to .008% and the Association of Swiss Chemists after the physiological experiments of Leuch, Schmitt, Schaffer and Bertschlinger raised the limit to .02%, total SO₂ of which not more than .002% might be free. This is the limit now adopted legally in Belgium, Spain, Switzerland and Germany. It is worthy of note, however, that these limits are not strictly enforced, as many of the finest and most highly prized wines of the Rhine considerably exceed them.

France in 1907 and the United States in 1902 (decision 76) raised the limit still further to .035% of which .007% might be

free. Finally, " Le Conseil, d'hygiéne publique de France," on the 27th of March, 1911, recommended a limit of 450 milligrams per liter or .045% of which .01% might be free.   This with a tolerance of 10% makes the maximum .05% and is based on the researches of the Bordeaux Commission which found .065% innocuous and whose conclusions were corroborated by the observations of Dr. Leuch of Zurich and of Rost and Franck in Germany.

These limits are more than sufficient for all purposes in most wines. Only in special cases such as with the *Botrytis* wines of the Sauternes and the Rheingau need they be equalled or exceeded. In fact there seems to be little cause for legal restrictions in this matter, as an excess of sulfurous acid will injure the quality and selling price of a wine before it reaches a point at which it becomes dangerous to health.   The main utility of these legal restrictions has been that it has caused the wine-makers to make a thorough study of the question and to determine the exact amounts of SO_2 and the best methods of application to produce the maximum good effect on the quality of their wines.

(b) *Amounts for various purposes.*   The amount of sulfurous acid which it is necessary to use varies within wide limits according to the purpose.   Leaving out of consideration the disinfection of cellars and casks, the greatest difference exists between the application of the acid before and after the fermentation of the sugar. Before fermentation, much more may be used, because a great part will disappear during the process and much more must be used, because, owing to the nature of the liquid, it is then much less effective.   In the wine, the effects of the sulfurous acid upon the micro-organisms is intensified by the acids, tannin and alcohol, while in the must the resistance of the micro-organisms is increased by the presence of sugar and abundant nutritive materials.

When sulfurous acid is added to must or fresh grapes a great part combines almost immediately with certain components of the juice and practically only that which remains free is effective. If we were to use as much after fermentation as we must use before, so much would remain free that the wine would be seriously injured.

In a general way, it may be said that approximately ten times as much SO_2 is necessary in the cases where it is used before fermentation as in those where it is used after. An approximate idea of the amounts needed for various purposes according to various authors is given by the following table.

TABLE I. Amounts of SO_2 for various purposes

Authority	Purpose	SO_2 per cent.
	After Fermentation	
Pacottet	Racking of old wine	0010 to 0025
Ventre	Racking of wine	0010 to 0050
	Before Fermentation	
Andrieu	Fermentation of red wine	0100 to .0200
Martinand	" " " "	.0300 to 0400
Ventre	" " " "	.0100 to 0500
Babo u. Mach	Preservation of must for 1 mo.	0500

The variations in the amounts to use for the same purpose according to these recommendations are as 1 to 5. Babo and Mach state that .05% will delay fermentation a month, while Ventre recommends the use of this amount in cases where delay is not desirable. The reason of these apparent discrepancies is that the effect of the SO_2 varies greatly with several conditions and particularly with the temperature and composition of the must and with the number and characters of the micro-organisms present.

(c) *Transformations.* When sulfurous acid is introduced into must or wine from any of the sources mentioned above, its form and amount undergo immediate and continued changes:

(1) Part unites rapidly with the aldehyde present;[1]

(2) Part unites in a similar way with the sugars and other constituents;

(3) Part oxidizes to SO_3 and forms potassium sulfate by replacing organic acids;

(4) Part evaporates on every exposure of the liquid to the air;

(5) Part remains as free SO_2.

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[1] M. Rocques, Annales de Chimie analytiques, 1897, p. 421.

The rapidity and extent of these changes vary greatly with conditions and can be foretold only approximately.

The combination with aldehyde takes place very rapidly. According to W. Seifert as quoted by Babo u. Mach[1], in the case of two wines aged 6 mos. and 3 years respectively, it was almost complete in one hour. In 24 hours, 12.8 m. g. SO_2 per liter had combined with the aldehyde in the young wine, and, in the old wine, which contained more aldehyde, 32.7 m.g.

The aldehydic combination is very stable and resists oxidation. It therefore persists even in old wines. It has a pleasing odor and some observers ascribe a part of the bouquet of certain wines to its presence.

The combination of the sulfurous acid with the sugar is of a similar nature. It takes place gradually, but, with moderate amounts (up to .01%) seems to be complete usually within 12 to 24 hours. The reaction is more rapid at higher temperatures.

The red color of the grape disappears on the addition of sulfurous acid owing to the production of a colorless combination with the pigment. This combination is unstable and the color reappears on the evaporation or oxidation of the SO_2. The regenerated color is very stable and cannot be removed by the ordinary treatment with bone charcoal. Repeated decolorization with SO_2 and regeneration by aeration will finally destroy the coloring matter, apparently owing to the formation of small quantities of H_2O_2, accompanying the change of SO_2 to SO_3.

The free SO_2 and its various combinations are more or less rapidly oxidized to SO_3. This oxidation is hastened by aeration and retarded by the presence of alcohol. The retarding effect of small quantities of alcohol are shown by the following tests made by Henry Fort[2].

TABLE II.   Effect of Alcohol in checking oxidation of SO_2

	Water Solution	Water and a little alcohol
Original % of SO_2	.242	.242
After 10 days.	.169	.224
After 20 days.	.122	.205

[1]Kellerwirtscgaft, p. 327, 1910
[2]Thesis° University of California, 1902.

In 20 days half of the sulfurous acid in the water solution has been oxidized but only one sixth where alcohol was present.

Tests by W. Cruess show that in weaker aqueous solutions all the SO_2 may be oxidized in two days and that this oxidation is restrained by the presence of tartaric acid.

TABLE III.   Effect of Tartaric Acid in checking oxidation of SO_2

Time	Water	Time	Water plus 5% Tartaric
Original % of SO_2	.01792	Original % of SO_2	.02100
1 hr.	.01574	45 hr.	.02100
25 hr.	.00512	75 hr.	.02100
49 hr.	none	93 hr.	.00640
		117 hr.	.00480

The tartaric acid thus preserved the SO_2 from oxidation under the conditions of the test, completely for 75 hours and only three quarters of it was oxidized in about 5 days.

The combined restraining effects of all the constituents of grape must are even greater.

TABLE IV.   Disappearance of SO_2 in Grape Must

Hours	Per cent. of SO_2
0	.01970
42	.01970
72	.01920
91	.01664
116	.01344
140	.01024
193	.00960

In this test only one half of the SO_2 had been eliminated by oxidation and other modes in 8 days, although fermentation had taken place in the meantime.   A determination of the sulfates will give us a fair measure of the amount of this SO_2 oxidized.

TABLE V.   Proportion of SO₂ oxidized during fermentation

	SO₂ in Must	Sulfates in new Wine	SO₂ corresponding to increase in sulfates
Laboratory tests in flasks			
1. Grape Must 20.5% B.	ʊ	.026%	
2. " " " "	.02%	.026%	
2. " " " "	.02%	.041%	.0055%
3. " " " "	.03%	.057%	.0116%
Winery tests in large vats			
1. Green Hungarina (white)	0	.043%	
2. " "	.019%	.058%	.0055%
1. Petite Sirah (red)	0	.045%	
2. " " "	.018%	.075	.0110%

In these tests from about one quarter to a little more than one half of the SO₂ appears to have been oxidized to SO₃. The increase of sulfates even in an extreme case is less than the natural variations between different grapes.

The difference between the amount of SO₂ which disappears from the must or wine and that which is found in the form of sulfates is accounted for by the vaporization of the gas and its escape into the air. The amount which escapes in this way amounted in the winery tests mentioned in the foregoing table to from ⅛ to ¼ of the total quantities used.

A portion of the SO₂ at first usually fails to escape, to oxidize or to form organic combinations. It remains in the active or free state for a time.

Where the sulfurous acid is used before fermentation the portion which remains free is only a small part of the whole but is extremely variable. The causes of this variability do not seem to have been well explained but it seems to be connected with varieties in the composition of the must. In must from over-ripe grapes very little remains free and this little disappears rapidly. In must from under-ripe grapes a larger proportion remains free

and this disappears more slowly. In most cases where moderate amounts of SO_2 are used in the must before fermentation, little or none is found free in the wine after fermentation and where a little does remain it disappears with time.

These facts are illustrated by the following tests by W. Cruess. Two musts were taken: one from ordinary fresh grapes somewhat under-ripe and showing 20°B — the other was an infusion of raisins and showed 24°B. To these musts were added various amounts of SO_2 in the form of $K_2S_2O_5$. The free SO_2 was determined immediately after the addition and subsequently at intervals during and after fermentation.

TABLE VI. Disappearance of free SO_2 from fresh Grape Must

of 20°B

Amount of $K_2S_2O_3$ added, 400 m.g. per liter, (equals .02% SO_2)

	Immediately after addition,	.0166% free SO_2	
24 hrs.	" "	.0094	" "
39 hrs.	" "	.0092	" "
113 hrs.	" "	.0071	" "
135 hrs.	" "	.0068	" "
168 hrs.	" "	.0060	" "
543 hrs.	" "	.0001	" "

TABLE VII. Disappearance of free SO_2 from Raisin Must of

24°B

Amount of $K_2S_2O_5$ added per liter — 3000 m.g. 1200 m.g. 400 m.g.

	Total SO_2.— 15%	.06%	.02%
Per cent. of free SO_2 remaining —			
On addition,	.02688	.01158	.00448
After 18 hours,	.02137	.00588	.00320
After 42 hours,	.01279	.00461	.00320
After 67 hours,	.00576	.00230	.00089

The contrast in the effects of the two musts is shown graphically by the following curves, drawn from the data of Tables VI and VII.
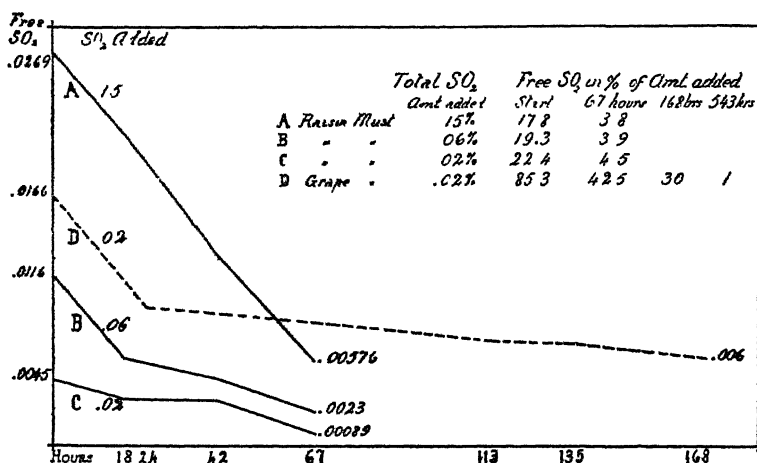
These curves show clearly the greater power of neutralizing the activity of the sulfurous acid possessed by the raisin must. Where equal amounts were added, the raisin must shows at first only 27% of the free SO_2 shown by the must of grapes which were barely ripe. Where the raisin must received three times this amount the free SO_2 is still 30% less. Even with seven and a half times the amount, the raisin must at first shows only 62% more than the fresh must and at 67 hours shows about 30% less.

This explains in part the need of larger amounts of sulfurous acid in fermentations in hot regions where the grapes are sweeter and often partially dried. It also explains the divergence of views as to the quantity of SO_2 necessary to restrain the activity of micro-organisms.

A raisin must to which was added 4000 m.g. per liter of $K_2S_2O_5$ (equal to .2% of SO_2) fermented readily after 75 hours, while a fresh must was kept from fermenting for 70 hours by the addition of only 300 m.g. per liter (.015% SO_2).

These differences in the activity of the SO_2 are due to differences in the form it assumes in the various media and is a complete

refutation of the claim that the form has no bearing on its action. When over 1000 m.g. of combined SO_2 per liter cannot restrain fermentation while 30 m.g. of free SO_2 can prevent it entirely we are not justified in concluding that because .5 grams of free SO_2 per day may sometimes produce headaches, that the same amount of combined SO_2 will be harmful. On the contrary, it makes it probable that very much larger quantities of the combined acid will be perfectly harmless.

(d) *Desulfitation*. The temporary preservation of must with sulfurous acid has long been practiced in many grape-growing regions. Such must known as *mistelle, agufrado*, etc., is used for the manufacture of certain sweet wines. Where it is necessary to ferment them they are freed from their excess of SO_2 by heating and aeration. This treatment gives the must a *rancio* or sherry taste and caramelizes some of the sugar, rendering it unfitted for the manufacture of dry wine.

Lately a modification of this method adapted for dry wine has been suggested and is said to have been applied successfully on a large scale in Algeria. The must or crushed grapes are sterilized and kept from fermentation by the use of very large quantities of sulfurous acid reaching 150 grams per hectoliter (.15%) in the case of very ripe grapes. Must treated in this way is said to keep without change from one vintage to the next and can be " desulfited " and fermented when convenient. The " desulfiting " is accomplished by aeration and by boiling at 70°C in a partial vacuum. In this way the SO_2 is displaced or destroyed without injuring the character of the must. It is claimed that wines made in this way are superior and free from all the defects of imperfect fermentations.

The sulfurous acid used is from 5 to 10 times the maximum amounts used in the ordinary sulfiting of wines and yet is said to result in a perfectly wholesome product. The method allows the fermentation to be spread over many months instead of being concentrated into a few weeks and makes their accurate control much simpler. If such large doses of SO_2 do not injure the finer qualities of the wine the method offers a remedy for many of the difficulties of wine-making.

4

IV. EFFECTS ON MUST AND WINE

The effects of sulfurous acid on must and wine are of two kinds:
(1) Those due to its direct chemical actions, and (2) Those caused
indirectly by its influence on micro-organisms and enzymes.
The latter are much the more important.

(a) *Micro-organisms.*   The various micro-organisms which
occur in must and wine possess widely different degrees of
resistance to the restraining powers of sulfurous acid. Among
the most sensitive are the bacteria, especially those forms con-
cerned in the production of wine diseases.   Many of the com-
mon molds, e. g., *Penicillium* and wild yeasts, e. g., *S. apicula-
tus*, which are more or less injurious, are sensitive to small
amounts. The ordinary wine yeast, S. ellipsoideus, in all its
varieties, is the most resistant of all the forms commonly en-
countered in the processes of wine-making.

These facts are shown by the following observations of W.
Cruess.

Two large vats were filled with Zinfandel grapes which had
been brought by rail from the San Joaquin valley. To one vat,
No. 1, was added 12 oz. per ton of potassium meta-bisulfite. The
other vat, No. 2, was fermented in the ordinary way without
additions. The character and relative numbers of the various
micro-organisms was determined in the must directly after
crushing and in the wine directly after fermentation by means of
gelatine-plate dilution cultures. The results were as follows:

Must No. 1, (sulfite and pure yeast) plates showed no mold or
    pseudo-yeasts.

Must No. 2, (no addition) plates showed almost nothing but
    penicillum and apiculatus.

Young Wine No. 1, (sulfite and pure yeast) plates showed nothing
    but wine yeast.

Young Wine No. 2, (no addition) plates showed molds and a
    mixture of various yeasts.

Two and a half months after fermentation No. 1, the sulfited
wine, was clear and showed a little sediment which the micro-
scope revealed to be principally old yeast cells mixed with a few
rod-shaped and paired bacteria.

At the same time No. 2, the ordinary wine, was cloudy and its more bulky sediment showed only a few yeast cells but large numbers of filiform and a smaller number of short bacteria.

A quantitative estimate was made on two other vats of similar grapes. Plates were made of the must as it ran from the crusher, again shortly after the addition of 8 oz. of sulfite per ton and finally shortly after the addition of a starter of pure yeast with the following results:—

TABLE VIII.   Number of Micro-Organisms per cubic cent.

	Wine Yeast	S. apiculatus	Pseudo Yeasts	Molds
Before sulfiting	20,000	2,830,000	30,000	1,600,000
After sulfiting	560,000	0	0	0
After addition of yeast	2,500,000	0	0	0

Many other tests of a similar character were made with uniform results. Before sulfiting, the Pseudo yeasts, molds and S. spiculatus were in such a majority as to make it difficult to find any pure yeast. After sulfiting, these relations were reversed. The injurious organisms were so far eliminated or destroyed that under the conditions of the tests none were found and the true wine yeast alone appeared.

The benefits of this favorable change in the micro-flora was manifested by a more rapid and complete fermentation of the wine, satisfactory clearing and the reduction of the development of the anaerobic bacteria to harmless limits.

This sensitiveness of injurious forms and the high resistance of the only useful form make it possible by a judicious application of sulfurous acid to obtain a fermentation which is practically a pure culture.

The elimination of all microbial activity except that of the wine yeast is the principal object of all the minute care necessary in the manufacture of fine wine. Now, while the use of sulfurous acid is not a substitute for this care, it is its necessary complement

and without it the most careful wine-maker must often fail in his endeavor.

The composition of grape must is very favorable to the development and activity of a large number of micro-organisms. A finished wine, owing to its complete defecation, i. e., absence of all suspended matters, its high attenuative, i. e., exhaustion of microbial nutrients and to the antiseptic qualities of its alcohol, acid and tannin is very unfavorable to their growth and almost proof against the attacks of most of them.

The chief function of sulfurous acid is, by the elimination, destruction, or paralysis of injurious micro-organisms, to protect the susceptible must until through the action of the yeast it is changed into the immune wine.

Sulfurous acid, therefore, as used in wine-making, differs essentially from all other anti-eptics in this: *The exercise of its antiseptic properties is temporary.* They are utilized only during certain stages in the manufacturing process and disappear completely from the wine before consumption. A good wine keeps perfectly. not because of any sulfurous acid it may contain, for that exists in an amount and in a form totally inadequate for this purpose, but because of its composition, attenuation, and the absence of micro-organisms.

It is in fact, *impossible to preserve* wine *with sulfurous* acid; for, if enough free SO_2 exists in a susceptible wine to prevent microbial deterioration, the wine is spoiled or rendered unmerchantable by this SO_2.

It is, therefore, incorrect to speak of sulfurous acid as a preservative of wine. It is no more a preservative in the ordinary sense of the word than are cleanliness, pasteurization or refrigeration, which, like it, are employed for the elimination or destruction of injurious micro-organisms.

Acquired resistance of yeast. If a small quantity of sulfurous acid is added to an unsterilized must containing yeast, the start of fermentation is delayed. The delay is slight with small additions, but increases with large amounts. This is shown by the following table.[1]

[1]Experiments made by R. W. Bettoli   Thesis 1911   University of California.

TABLE IX. Delay of Fermentation with various additions of

SO₂

M. G. per L. SO₂	(HOURS)				
	Start	Finish	Delay	Net Time	Net Loss
0	19.5	211.5	0	192.	0
10	23.0	211.5	3.5	188.5	0
50	23.0	211.5	3.5	188.5	0
75	43.5	211.5	24.0	168.0	0
100	43.5	281.5	25.0	238.0	70
150	70.5	310.0	51.0	239.5	99
200	91.5	336.5	72.0	235.0	125
250	135.5	360.5	119.0	222.0	149

Up to an addition of .0075% under the conditions of the experiment the delay in the start of fermentation is counter-balanced by a greater rapidity after the start. In all cases up to .025% the fermentation was finally complete.

Facts of this nature were at one time supposed to indicate that sulfurous acid up to a certain dose increased the fermentative activity of the yeast and that yeast gradually acquired an increased resistance to its antiseptic effects.

With regard to the first point it seems probable that the acceleration of the rate of fermentation is due not to a change in the activity of the yeast but to the elimination of competing micro-organisms, whose excretions are known to weaken the activity of wine yeast. In fact, tests by W. Cruess show that the larger quantities of SO₂ used, notably decrease the power of the yeast to promptly and completely destroy the sugar.

The apparent increase of resistance was supposed to be due to natural selection by the multiplication of certain cells having a greater resistance than their fellows. Now, while various yeasts do differ in the degree of their resistance to SO₂, and, while there is an undoubted selection of this nature in a mixed culture, there

is evidence that the resistance of any race of yeast is constant and the apparent increase of resistance is due, not to changes in the yeast, but to changes in the form of the SO₂.

This is shown clearly by investigations of Martinand who found that beer yeast would cause fermentation in an artificial medium to which .05% of sulfurous acid had been added but not until all the *free* SO_2 had disappeared. Wine yeast, which is more resistant, he found would cause fermentation when the free SO_2 had fallen to .0025% but would not develop in the presence of more than .003%.

W. Cruess has found that a yeast will ferment in the presence of .19% of combined SO_2, but not in the presence of .004% of free SO_2, indicating that the antiseptic activity of free SO_2 is about fifty times as great as that of the combined form.

The delay of fermentation, therefore, is due to the presence of free SO_2 and its start to the vaporization, oxidation or combination of the acid.

The practice, therefore, of adding the sulfurous acid in fractional doses during the course of the fermentation is wrong. The best way is to add the whole amount at once to the crushed grapes or must before fermentation has started. Then, after a delay of 6 to 12 hours, to add yeast which has been propagated with little or no sulfurous acid. In this way the maximum antiseptic effect is exerted on the undesirable micro-organisms present in the must. On the other hand, the yeast is uninjured by contact with free SO_2 and entering the must in full vigor has no difficulty in completing its work before any of its competitors have recovered.

(c) *Oxidation.* Fermented wine is fit for consumption only after it has undergone certain changes comprehended under the term " aging." The phenomena of aging are due principally to slow oxidation. If oxidation is prevented entirely by storage of the wine in glass bottles or other impervious vessels, aging is arrested. On the other hand, if oxidation is excessive by reason of the composition of the wine or methods of handling, the phenomena of aging are exaggerated and the wine deteriorates rapidly in color, odor and taste, becoming vapid and decrepit.

Wines vary greatly in the rapidity and intensity with which they oxidize. High acidity moderates and retards the action while the presence of oxydase accelerates and intensifies it.

Oxydase occurs in more or less amount in nearly all grapes. It is more abundant in moldy grapes and especially in those attacked by the so-called " Noble Mold," *Botrytis cinerea*. The finest wines of the Rhine and of Sauternes are made from grapes on which this mold has reached an advanced degree of development. Such grapes contain large amounts of active oxydase and if not handled properly the resulting wine spoils rapidly.

Sulfurous acid offers a means of controlling the oxidation in all cases with great perfection and even of curing to some extent the results of over-oxidation. Wines which have become yellow, rancio and vapid from over-oxidation may be restored by sulfuring, if the deterioration has not gone too far. It is in preventing these defects that it is most useful, however. Where no sulfurous acid is used these defects always occur with more or less intensity. They can be prevented by proper and accurate sulfuring. In the racking of old wines a very light sulfuring of the cask modifies the effects of the aeration and prevents loss of bouquet. With younger wines a little more should be used, while with young wines made from moldy grapes or from those attacked by Botrytis comparatively large amounts are necessary.

The finest wines of the Rheingau and Sauternes could not be made without sulfurous acid. It is not used, as had been stated by those unfamiliar with the facts, to preserve the sugar. This could be accomplished by pasteurization. Its use is to prevent the injurious action of the oxydase. For this purpose no practicable substitute has been found.

Aging cannot be prevented altogether by the use of SO_2. As has been shown by Laborde[1], the oxygen present is taken partly by the SO_2 and partly by the oxidizable constituents of the wine.

(d) *Extract.* An increase of extract has been frequently noted in wines fermented with sulfurous acid. The sulfates due to the oxidation of the SO_2 is but a minute portion of this increase, which may reach .7%.

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[1] Revue de Viticulture, No. 860, p. 624.

According to Martinand the increase is due to the solution of pectates, but J. Ventre ascribes it to longer maceration. The preservation of the fixed acids will account for a portion of it. Dupont[1] has noted also an increase of ash amounting to .038% which is in great part, without doubt, due to the sulfates. The phosphoric acid, however, is also increased notably.

The changes in these respects are all favorable, tending to improve the quality and the composition ratios of the wine.

(e) *Acidity*. The most notable and most valuable influence on the composition of the wine is that shown by the fixed and volatile acidity. When grape must is fermented without the use of sulfurous acid there is always a diminution of the fixed acidity which may reach .2% or nearly 25% of the total. This loss is much diminished or eliminated when sulfuring before fermentation is practiced.

The small quantities of malic and citric acid in ripe grapes disappear in an ordinary fermentation but are found intact in the wine fermented with SO_2.

Corresponding to the decrease of fixed acids there is always a formation of volatile acids. In sound wines this should not amount to over .1%. In defective fermentations it may be nearly double this. Some of the volatile acidity is due to the normal activity of the yeast. Where excessive, the excess is due to the growth of wild yeast and bacteria or to an abnormal or unhealthy condition of the yeast. Where sulfurous acid is used before fermentation, the volatile acid is always lower. In practice it is from .02% to .04% lower in successful fermentations. The difference may be even greater when the absence of SO_2 results in a defective fermentation.

In hot climates, the fixed acidity of the grapes is one of their most valuable constituents and it is often increased by the addition of tartaric or citric acid. Such additions are usually unnecessary where sulfuring is practiced. In all climates, there is a close connection between the keeping quality of a wine and the lowness of its volatile acidity.

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[1] E. Dupont, Revue de Viticulture, No. 873, p. 255.

(f) *Alcohol.* The increase of alcohol is usually at least .1% and may be much more. It is due principally to the removal of molds and wild yeasts, especially of S. apiculatus, which destroy sugar with the production of little or no alcohol. Fermentations of pure yeast in sterilized must show the same alcohol whether SO_2 is used or not.

Where large increases of alcohol occur, as sometimes happens, they correspond to remnants of unfermented sugar. Where sulfurous acid is not used, especially in hot climates, the growth of bacteria and the resulting volatile acids trammel the work of the yeast so that it is unable to convert all the sugar.

(g) *Color.* Sulfurous acid makes unstable colorless components with the coloring matter of grapes. A pink wine may be rendered white by sulfuring. With time and aeration, however, the color reappears. The regenerated color is very stable. A pink wine can be decolorized by treatment with bone charcoal. One in which the color has been removed by SO_2 and regenerated by aeration is more difficult to decolorize in this way. Repeated sulfurings followed by aerations will, however, finally destroy the coloring matter. This, according to Chabert, may be due to the formation of minute quantities of H_2O_2 during the oxidation of SO_2 to SO_3.

The higher color of red wines fermented with sulfurous acid cannot all be accounted for by an increase of stability. The wine from a sulfited vat is usually more deeply colored than that from one otherwise identical which has received no sulfites. This seems to be due to a greater solubility of coloring matter in the presence of sulfurous acid. Experiments by Martinand[1] confirm this view:—

1. Grapes were macerated with 50 to 500 m.g. per liter SO_2 Must separated and fermented.

2. Same grapes were fermented without SO_2.

3. Same grapes were fermented on skins with 200 to 500 m. g. per liter SO_2.

[1] Revue de Viticulture, No. 854, p. 452.

The wine (1) made from must extracted from grapes macerated with 500 m.g. SO₂ showed as much color as that made by fermentation on the skins (2) without SO₂.

(h) *Quality.* The influence of the use of sulfurous acid on the general quality of the wine must be considered from two points of view. First, as regards its effect on the chemical composition. These are definite and capable of quantitative determination. Second, as regards its effects on those more delicate but no less important characteristics on which the organoleptic tests of the expert taster pass final judgment.

So far as chemical analysis is concerned, the evidence is both favorable and unanimous. There is no evidence whatever that the use of sulfurous acid has any influence on the composition that is not beneficial. The alcohol, extract, ash and color are increased in nearly all cases, the destruction of the fixed acids and the production of volatile acids are prevented or decreased. These facts have been demonstrated repeatedly by laboratory experiments corroborated by tests on an industrial scale. The effects are all of the same character as those which follow special care in the management of the fermentation, particularly in cleanliness and the control of temperature; they are in fact the results of a pure fermentation. The most constant effects are the decrease of volatile acid and the increase of color. In both these respects the contrast is the greater the longer the wines are kept. The increase of the color of red wines is particularly marked and seems to be due partly at least to a direct chemical action on the coloring matter.

With regard to the organoleptic tests, the evidence is almost equally unanimous but there are a few dissenting opinions on some points.

The microscopical examination is always favorable to the sulfited wines. The absence of notable numbers of bacteria indicating soundness and good keeping qualities. This is co-ordinate with the low contents of volatile acid. The clearing of the wine is always more rapid and satisfactory. The bouquet and flavor of the wine are fuller and cleaner. The only defect which has been noted is a certain greenness or harshness of certain wines especially of wines made from imperfectly ripe grapes. It is due

to the integral conservation of the fixed acids which is one of the main advantages in hot climates and with perfectly mature grapes.   It would be a mistake, however, to conclude that no sulfurous acid should be used with grapes of high acidity.   To allow molds, wild yeasts, and bacteria to diminish this acidity would introduce defects much more serious than an excess of fixed acidity.   Less sulfurous acid should be used because less is effective but the natural acidity should be reduced if necessary by other means than the growth of the germs of wine diseases.

A favorable decision with regard to the use of sulfurous acid in wine-making does no' involve a belief in its indiscriminate or excessive use.   It is only by the careful use of amounts accurately calculated for each case that the full benefits of the practice can be obtained and its dangers avoided.

LES VINS BLANCS DE LA MOSELLE ET DU RHIN

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Les propriétaires viticulteurs et bien davantage encore les Négociants en vins de la Gironde n'ignorent pas la très grande vogue qu'ont eue pendant bien des siècles en Angleterre spécialement les vins de la région bordelaise.

Aujourd'hui, ils savent tout aussi bien que, depuis quelques années déjà, les consommateurs de la Grande Bretagne ont une tendance, en place de nos Bordeaux rouges, à augmenter leur préférence pour le Porto à haut degré, ou à les remplacer par du Whisky (eau de vie d'orge) qu'ils mouillent selon leur goût avec de l'eau ordinaire ou avec de l'eau gazeuse.

L'hygiène d'aucun pays n'approuvera assurément une pareille substitution.

Quant aux vins blancs de degré alcoolique moyen, comme le sont les nôtres le public anglais a une propension à suivre deux modes: Les indépendants de la médecine inclinent vers les vins du Rhin: les autre, ceux qui n'agissent qu'avec le conseil de leur médecin, adoptent plutôt les vins de la Moselle. Pour appuyer leur avis, les membres du corps médical prétendent, qu'à cause de la faiblesse de leur acidité générale, ces derniers vins conviennent mieux aux estomacs délicats, qu'ils sont plus hygiéniques.

Comme cet argument fait feu de file et est le plus souvent opposé par les consommateurs anglais à ceux qui leur offrent nos Bordeaux; et comme aussi on a plusieurs fois sollicité notre avis à ce sujet, nous avons tenu à vérifier jusqu'à quel point ces deux courants du gôut anglais pouvaient être fondés.

Dans ce but, nous nous sommes procuré une douzaine de bouteilles de ces vins, la moitié de la Moselle, le reste de la région du Rhin.

La maison de Coblentz qui les a fournis est réputée la plus honorable du pays; et la mise à l'épreuve qu'elle a subie depuis de longues années autorise à avoir confiance dans l'authenticité des origines indiquées.

Ces vins soumis à l'analyse générale ordinaire ont fourni les résultats suivants:

<div align="center">MOSELLES</div>

<div align="center">Vins blancs de la Moselle</div>

	Erden 1909	Graach 1909	Grünhausen 1906	Zeltingen Himmelreich 1907	Berncastel Rosenberg 1908	Vinningen 1908	Moyenne
Densité	992	992	992	990	995	990	
Degré alcoolique	10.6	12.0	12.9	12.0	12.95	12.6	12.1
Alcool par lit. gr.	84.5	95.4	102.6	95.4	102.6	100.2	12.1
Extrait sec à 100° par lit. gr.	18.75	20.00	24.25	18.5	30.10	18.50	21.68
Extrait réduit par lit. gr.	17.65	18.40	22.00	17.15	21.10	16.10	18.73
Extrait densimétrique par lit. gr.	17.20	19.40	22.70	17.30	26.00	17.50	20.01
Sucre réducteur	2.10	2.60	3.25	2.35	10.00	3.40	3.95
Sulfate de potasse par lit. gr.	0.58	0.62	0.65	0.49	0.51	0.49	0.55
Rapport $\left\{ \begin{array}{c} \text{alcool} \\ \text{extrait réduit} \end{array} \right\}$ gr.	4.68	5.18	4.66	5.53	4.86	6.24	0.55
Acidité totale en SO$_4$H$_2$ gr.	5.00	4.83	5.75	4.78	6.10	4.14	5.10
Acidité volatile SO$_4$H$_2$ gr.	0.55	0.59	0.64	0.44	0.49	0.40	0.52
Acidité fixe SO$_4$H$_2$ gr.	4.45	4.24	5.11	4.34	5.61	3.74	4.58
Somme alcool + acidité totale	15.60	16.83	18.65	16.78	19.00	16.74	4.58
Somme alcool + acidité fixe	15.05	16.24	18.01	16.34	18.51	16.34	4.58
Tartre corresp. à potas. totale	3.06	2.83	2.70	2.75	2.64	2.78	4.58
Tartre corresp. à ac. tartri.	2.78	2 70	3.40	2.78	2.83	1.74	4.58
Acide tartrique libre	0.00	0 00	0.56	0.00	0.15	0.00	4.58
Cendres	2.00	1.50	1 75	1.75	2.00	2.00	4.58
Dégustation	très tr. aci	très tr. aci	très acide	acide	très acide	acide	4.58
Rapport $\left\{ \begin{array}{c} \text{alcool degré} \\ \text{acidité fixe} \end{array} \right\}$	2.38	2.82	2.83	2.75	2.30	3.34	4.58
Corresp. à degré alcool	9°4	10°	10°	10°	9.2	10°7	9°9
Déviation saccharimétrique	<0.20	0.00	<0.25	000	<5	<0.5	9°9

Hocks

Vins blancs du Rhin

	Hallgarten 1908	Bodenthal 1908	Rüdesheim 1908	Deidesheim 1907	Nac-Kenheim 1908	Nierstein 1908	Moyenne
Densité	993	993.5	995	995	996	992	"
Degré alcool	12.70	11.50	11.40	12.40	10.40	11.50	11.65
Alcool par lit. gr.	101.00	91.40	90.60	98.60	82.70	91.40	11.65
Extrait sec à 100° par lit. gr.	24 20	20.70	23.70	29.00	25.70	19.00	23.71
Extrait réduit par lit. gr.	22 90	19.30	22.10	27.50	25.30	18.40	22.58
Extrait densimétrique par lit. gr.	23.80	20.50	23.10	28.70	25.00	18.80	22.58
Sucre réducteur	2.30	2.10	2.30	2.50	1.40	1.60	2.03
Sulfate de potasse par lit. gr.	0.80	1.30	1.30	1.00	0.70	0.98	1.01
Rapport { alcool / extrait réduit } gr.	4.41	4.73	4.10	3.58	3.26	4.96	1.01
Acidité totale en SO_4H_2 gr.	4.90	4.40	5.10	5.46	6.10	4.10	5.00
Acidité volatile gr.	0.40	0.58	0.58	0.56	0.50	0.45	5.00
Acidité fixe gr.	4.50	3.82	4.62	4.90	5.60	3.65	5.00
Somme alcool acidité totale gr.	17.60	15.90	16.50	17.86	16.50	15.60	5.00
Somme alcool acidité fixe	17.20	15.32	15.02	17.30	16.00	15.15	5.00
Tartre corresp. à potasse	2.83	3.11	3.86	5.13	4.62	3.11	5.00
Tartre corr. à acide tartrique	2.16	2.08	2.00	1.14	1.89	2.13	5.00
Acide tartrique libre	0.00	0.00	0.00	0.00	0.00	0.00	5.00
Cendres	2.10	2.00	2.50	2.90	2.50	2.00	5.00
Dégustation	tr. aci	acide	tr. aci	acide	tr. aci	acide	
Rapport { alcool degré / acidité fixe }	2.82	3.01	2.52	2.53	1.85	3.15	
Corresp. à degré alcool	10 °	10 °2	9 °50	9 °50	8 °3	10.50	9.7
Déviation saccharimétrique	0.00	0.00	0 °5>	0.50>	0.50>	0.00	

Discussion des Résultats

Vins Blancs De La Moselle

Leur degré alcoolique est en moyenne de 12.1 avec 10.6 comme plus bas et deux fois 12.9 comme plus haut. C'est un peu plus élevé que dans nos vins de qualité analogue[1] et égal au degré de nos grands vins blancs.

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[1]D'après l'avis des négociants compétents, tous ces vins Moselle et Rhin correspondent à nos cinquièmes crus girondins.

L'extrait réduit est en moyenne de 18.75 gr. par litre avec 16.10 et 22 comme extrêmes; c'est-àdire avec beaucoup d'irrégularité dans le corps, dans la chair, ainsi que le disent les dégustateurs.

Le sucre réducteur ou de fruit est en moyenne de gram. 4.00 avec 2.10 comme plus bas et 10.00 comme plus haut: encore irrégularité fréquente dans les vins de cette origine, par suite des caprices qu'y manifeste le soleil.

Le sulfate de potasse est de 0 gr. 55 par litre en moyenne, sans grands changements dans la série.

L'acidité totale, traduite selon l'usage français en acide sulfurique, va par litre de gram. 4.14 à 6.10 avec une moyenne générale de 5.10.   C'est assurément supérieur au degré de l'acidité moyenne de nos vins de qualité analogue et d'âge pareil.

L'acidité volatile est, en général, bonne pour l'âge des vins.

L'acide tartrique libre s'y rencontre deux fois, dont une en proportion sensible.

Les rapports alcool degré: acidité fixe correspondent tous à des degrés d'alcool inférieurs à ceux qui ont été réellement trouvés.   Cette infériorité est en moyenne de deux degrés et les rend suspects *d'un vinage de deux degrés effectifs.*

Vins Blancs Du Rhin

Le degré d'alcool oscille entre 10.40 et 12.70 avec 11.65 en moyenne.   C'est un peu plus faible que les Moselle.

L'extrait sec réduit est par litre en moyenne de gr. 22.58 avec 18.40 et 27.50 comme proportions extrêmes.   Bon rendement moyen, mais grande irrégularité.

Le sucre réducteur ou de fruit va de 1.40 à 2.50 avec une moyenne de gram. par litre 2.03.   A cette dose ce sont des vins secs.

Le sulfate de potasse va de 0.70 à 1.30 avec moyenne de 1 gr. par litre; proportion bien acceptable pour des vins blancs vieux.

L'acidité totale, (toujours traduite en acide sulfurique) monte de gr. 4.10 par litre à 6.10 avec moyenne de 5.01.   C'est le même dosage et avec les mêmes écarts que pour les Moselle.   Semblables critiques leur sont applicables.

L'acidité volatile est régulière et normale.

Les rapports alcool degré: acidité fixe donnent lieu ici à de pareilles observations que pour les Moselle.   .

Resume

La constitution de ces deux espèces de vins est assez rapprochée elle est de part et d'autre assez irrégulière.

Les points les plus saillants sont: L'élévation relative du degré alcooli que et aussi celle de l'acidité totale des deux côtés.   Voilà pourquoi pour les vrais dégustateurs, tous ces vins manquent de souplesse et laissent un sentiment de verdeur et d'acidité.

Il est entendu que les viticulteurs qui les produisent et les négociants qui les soignent n'en peuvent mais.   La cause première est dans le climat, incapable de produire des raisins pareils à ceux de la Gironde parce que le centre du Sud-Ouest français possède sur ce point, en dehors de toute autre qualitè oenologique un climat absolument privilégié.

Conclusion

Il est possible que les vins du Rhin et ceux de la Moselle dont nous avons analysé les types ci-dessus arrivent à convenir mieux que nos Bordeaux à certains estomacs anglais.   C'est affaire de mode ou d'éducation de gôut pour les premiers et de simple suggestion médicale pour les seconds.

Mais il est bien entendu que la vérité ne permet pas de dire que cela tient à une constitution mieux équilibrée, moins acide et plus hygiénique que dans nos bordeaux, vu que l'expérience démontre que c'est entièrement l'opposé.

THE RELATION BETWEEN THE OPTICAL ROTATION AND THE FERMENTABILITY OF ACID CONVERTED STARCH PRODUCTS

By Geo. Defren

Newton, Mass.

It is well known that "dextrin"—so-called—is but little fermented by yeasts, especially the ordinary variety of Sac. Cerevisiae. When fermentation does occur, it is generally found to be due to the fact that the "dextrin" has been considerably hydrolysed, as would be apparent when its optical and reducing properties were investigated.

We also know that malt worts, made by saccharifying starch with diastase at high temperatures, do not ferment as far as do those which have been produced at lower temperatures. This is due to the fact that more maltose is present in the latter. Dextrose and maltose ferment easily, while the higher molecular complexes—the so-called "malto-dextrins"—do not do so with ordinary brewer's yeasts. In other words, diastase converted starch products of higher optical rotation ferment less than do those of lower rotation under the same conditions.

As our knowledge of the composition of acid converted starch products has been considerably elucidated, it was considered of interest to investigate the question of the fermentability of such products, by subjecting glucoses of different optical rotations to the action of yeast.

It has been shown[1] that acids hydrolyse starch by producing first malto-dextrins, which then break down into maltose, and the latter finally goes over into dextrose. For convenience a chart of what occurs is inserted. It must be understood that this chart does not mean that at any specific optical rotation, the quantities of dextrin or maltose indicated, represents such to occur in a "free" state. There is plenty of evidence to warrant the conclusion that much of the dextrin and maltose present are

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[1] Jour. Am. Chem. Soc. XVIII. No. 10.

there in the form of molecular complexes, although "free malt-ose" is also in solution as has recently been shown.

PERCENTS

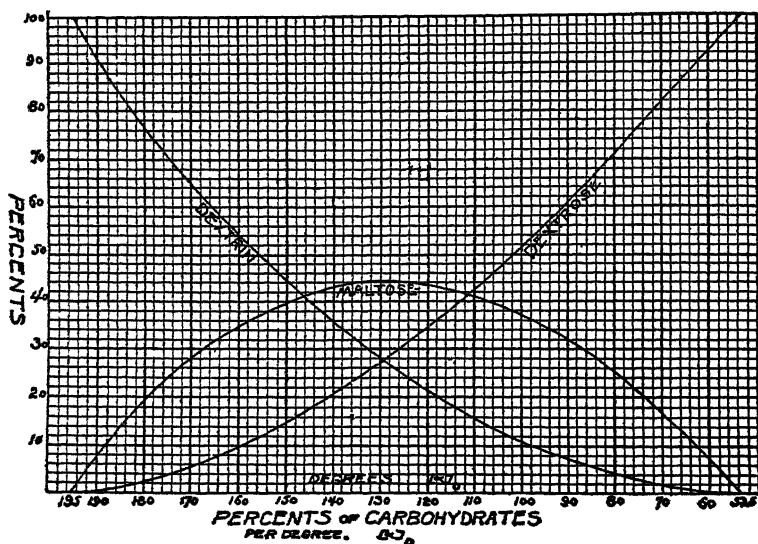PERCENTS of CARBOHYDRATES
PER DEGREE.

PLATE A

Samples of different optical rotations were prepared by hydro-lysing starch with acid in an autoclave.   The most satisfactory nutrient medium was found to be a mixture of yeast water-made by adding 20 grams of ordinary yeast in small amounts to a liter of boiling water, allowing to simmer for two hours, settling and filtering and a small percentage of Ammonium Phosphate.

Ordinary brewer's yeast—but not "pure cultures"—were used. The infection by lactic acid bacteria was less than 1%, and, with the work in hand, their effect was negligible.

Considerable difficulty was experienced in obtaining reliable values for the optical rotations after the samples had been fer-mented, and the alcohol had been evaporated.   This is due to soluble salts and optically inactive organic nutrient material, whose effects, while of little moment at high rotations are very much increased near the dextrose end of the curve (see plate A), where the unfermented residue is small.   The upper part of the

curve representing the optical rotation after fermentation is pretty well defined, but that obtained at lower rotations is still too ragged and incomplete to include it here. It is hoped to investigate this problem further, as well as to look into the nature of the unfermented residues from their copper reducing values.

A summary of results is given below. These are shown graphically in the plot following.

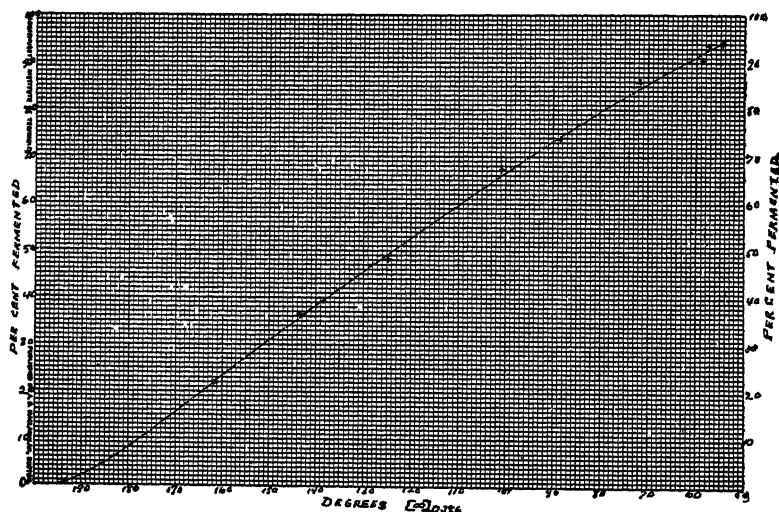| Original optical rotation $[\alpha]_{D356}$	% Carbohydrate fermented
180	6.2
162	21.4
144	36.1
139	38.8
125	48.2
101	67.3
89	73.5
71.7	86.3
59.1	90.2
57.8	94.1
55.3	93.8

PLATE B.

That there is a well defined " curve of fermentability " of acid converted starch products by yeasts is evident from the above. At higher rotations the maltose is probably in combination largely with dextrin, in such a form as to be only partially fermentable. This result is analogous to that obtained from diastase converted starch products. At the dextrose end of the curve we find the carbohydrates present almost entirely fermented. As all normally converted acid starch products color considerably below $[\propto]_D 90°$, and are decidedly dark between $[\propto]_D 65°$ and $[\propto]_D 53°.5$, it is safe to assume that some decomposition of dextrose has taken place. Some writers refer to this as " reversion." To what extent this occurs we do not know, but it is evident that the decomposition products of dextrose do not ferment entirely.

The writer is greatly indebted to L. C. Shaw and Hans C. Holm for preliminary work done on this subject.

SUR LA DÉTERMINATION DE LA VALEUR DES MASSES FILTRANTES POUR LA FILTRATION DE LA BIÈRE

Par M.M. A. Fernbach, Directeur, J. Crolbois, Chef de Laboratoire

A l'Ecole de Brasserie de l'Institut Pasteur, Paris, France

La filtration de la bière a pris dans ces dernières années un développement considérable qu'elle n'avait pas autrefois, par suite des exigences croissantes du public, qui n'accepte qu'un liquide parfaitement brillant. On ne filtrait autrefois que la biére de fermentation basse et même on soutirait directement du foudre tout le liquide qui avait une limpidité suffisante pour être livré tel quel à la consommation; actuellement, on filtre la totalité de la bière débitée et la filtration s'est même étendue récemment à la bière de fermentation haute, qu'on clarifiait précédemment par collage seulement.

Les filtres eux-mêmes ont fait l'objet de perfectionnements considérables; mais, en ce qui concerne les pâtes employées comme masse filtrante, en dehors de quelques conditions qu'elles doivent remplir, notamment celle de ne renfermer aucune substance soluble dans la bière et de ne lui communiquer aucune saveur, on ne s'est guère préoccupé, à notre connaissance, de mesurer d une manière précise leur valeur comme matière filtrante, c'est à dire ce qu'on peut appeler leur *pouvoir filtrant*. Lorsqu'un brasseur essaye une masse filtrante qui lui est offerte par le commerce, c'est par des moyens purement empiriques, c'est à dire par un essai de filtration.

Il est clair que cette méthode qui ne renseigne que sur une masse filtrante déterminée, et qui peut conduire à des pertes notables de bière si la masse est défectueuse, devient inapplicable lorsqu'il s'agit de comparer les valeurs de diverses masses, parce qu'elle exigerait qu'on eût à sa disposition un volume considérable d'une bière toujours semblable à elle-même au point de vue

de la composition et du trouble, et qu'il faudrait des essais prolongés pour obtenir des résultats comparables.

Le problème de la détermination de la valeur relative de diverses masses filtrantes s'étant posé à nous, nous avons imaginé pour le résoudre un appareil et une méthode qui font l'objet de la présente note. Noûs avons eu à comparer entre elles et avec des masses filtrantes existant dans le commerce des pâtes à papier en cellulose pure provenant des Papeteries bien connues de Vidalon, à Annonay (Anciennes manufactures Canson et Montgolfier).

Principe de la Méthode

Pour pouvoir comparer entre elles diverses masses filtrantes, il faut, de toute nécessité, qu'un même liquide soit filtré au travers de ces diverses pâtes dans des conditions identiques, c'est à dire sous une pression constante et toujours la même, et au travers d'une couche de pâte de même poids et ayant subi la même compression.

Appareil Employé, et Mode Opératoire

L'appareil représenté par le dessin ci-joint se compose essentiellement d'un cylindre en laiton dans lequel peut glisser à frottement doux un plateau perforé D, faisant office de piston. La tige E de ce piston est creuse et sert à amener le liquide à filtrer. Elle peut recevoir sur son extrêmité supérieure un plateau G, qu'on charge de poids, de manière à exercer sur la masse filtrante placée au-dessous du piston telle pression que l'on désire, et à constituer ainsi un gâteau de pâte à filtrer ayant subi une compression déterminée.

Le fond I du cylindre A porte un tube K par lequel s'écoule le liquide filtré. Sur ce fond repose une bague B mobile, portant une toile métallique *b'*.

Dans le cylindre, muni de son fond en toile métallique, on verse la masse obtenue en délayant 5 grammes de pâte à filtrer dans 200 centimètres cubes d'eau. On met ensuite en place une bague C, qui entre dans le cylindre à frottement doux, et porte, comme B, une toile métallique *c'*.

Par dessus cette bague, on entre le piston dans le cylindre, et on visse le fond supérieur L du cylindre. Ce fond est surmonté d'une presse-étoupe H, dans lequel passe librement la tige creuse du piston. Cette tige porte deux oreilles ajourées P, qui sont traversées par deux tiges filetées, M et M', servant de guides.

Les choses étant ainsi disposées, on charge le piston avec un poids déterminé, qu'on laisse agir librement pendant un temps choisi toujours le même. Pendant cette compression, une partie de l'eau retenue par la pâte à filtrer s'écoule par le tube K. On amène alors les écrous moletés N et N' au contact de la pièce P pour fixer le piston D dans sa position de descente, et on serre cette même pièce à sa face supérieure par les écrous moletés n et n'. Le presse-étoupe H est ensuite descendu à fond de course sur la rondelle qui forme joint, de manière à le rencre ètanche.

Le tube de caoutchouc qui prolonge la tubulure K étant serré par une pince à vis, il ne reste plus qu'à remplir le filtre avec le liquide à filtrer. A cet effet, la tige creuse E est mise en relation, à l'aide d'un tube de caoutchouc, avec le récipient contenant le liquide, et on laisse pénétrer celui-ci jusqu'à ce qu'il sorte par le petit robinet de purge R, placé sur le fond supérieur du cylindre.

Ouvrant alors l'orifice K, on laisse écouler le liquide filtré pendant un temps donné toujours le même, au bout duquel on recueille ce qui s'écoule dans un vase jaugé, afin de mesurer ce qui filtre pendant un intervalle de temps fixé à l'avance.

Le diamètre du cylindre de l'appareil décrit ci-dessus a été choisi de telle sorte que la surface filtrante du gâteau de pâte soit exactement de 10 centimètres carrés.

Pour chaque expérience nous employons, comme nous l'avons déjà dit, 5 grammes de pâte sèche, qui sont délayés dans 200 centimètres cubes d'eau. Après 10 minutes de contact, on agite fortement pendant 5 minutes, et on verse e mélange dans le cylindre de l'appareil.

Le piston est chargé d'un poids de 4 kilos, qu'on laisse agir pendant 15 minutes. On peut évidemment employer un poids différent, pourvu qu'on emploie le même poids pour tous les échantillons de masse filtrante à comparer. On peut également faire varier la pression sous laquelle le liquide est admis dans le filtre. Dans nos expériences, nous avons employé une pression

représentée par une colonne de bière de 2 mètres; la constance de la pression était obtenue en plaçant la bière à filtrer dans un flacon de Mariotte.

Quelques Chiffres Expérimentaux

Les chiffres suivants, que nous donnons à titre d'exemple, sont les moyennes de quatre expériences concordantes. Ils représentent le *pouvoir filtrant*, c'est à dire le nombre de centimètres cubes qui traverse notre filtre pendant 15 minutes, après qu'on l'a laissé fonctionner pendant 2 minutes avant de recueillir le liquide à mesurer.

Désignation des pâtes à filtrer	Pouvoir filtrant
A	1060 .
B	1015
C	640
D	679
E	890
F	1400

Il faut remarquer que les conditions de filtration dans lesquelles ont été faites ces expériences ne diffèrent pas beaucoup de celles de la filtration pratique de la bière. Dans tous les cas, elles sont rigoureusement comparables, et il serait très désirable que notre méthode ou une méthode analogue fût employée dans les laboratoires de brasserie pour le contrôle de la valeur des masses filtrantes.

ANALYSIS OF HOPS, AS BASIS FOR THEIR VALUATION

By Alfred Fischer

Milwaukee, Wis.

In a previous paper entitled "Modern Methods of Hop Analysis," I have given the results of a number of experiments on the correctness of certain methods for determining the more valuable constituents of hops. A number of the more common methods of hop analysis were compared. In the determination of the percentage of soft resins—the most important constituent—the methods most commonly employed are the titration method, also known as the Neumann method, and the direct method, described in the above named paper as the Milwaukee method. As I have shown, both methods furnish reliable results. Likewise was found the determination of hard resin in determining the ratio of hard resin to soft resins.

The soft resins, from the standpoint of modern hop investigation, must now be considered the most important constituent of hops, as far as brewing value is concerned.

The determination of tannic acid, once considered a very important factor in the valuation of hops, has been abandoned as being only of secondary value. The volatile oil is still considered by many of great influence on the taste and aroma of the beer. This topic, however, I shall treat later in this paper.

While there is more or less dispute about all these constituents among hop examiners and brewers, the fact is conceded that it is the soft resins which are soluble in water and beer that impart the characteristic bitter taste and for preservative action.

The results of the chemical analysis, the physical examination and the practical brew tests did not always agree. Two samples of hops, with the identical resin contents, did not always have the same physical qualities nor did they produce the same effects in wort and beer. The soft resins of hops are not simple bodies, and already Hayduck separated two principles, Alpha and Beta resin. Later investigators have studied the properties of these

two substances closely, and methods have been devised for their determination. However, as the investigations of others and the results of my experiments, given in the former paper, show, these substances separately do not permit us to judge the brewing value of hops in a reliable way, and their separate determination was therefore abandoned. It is evident that these compounds are easily changed, and, in fact, are constantly changing during curing, storage and even in the process of manufacture of wort and beer. It appears that they are slowly oxidized and are partly unsaturated compounds of the hydro-carbon nature. I considered it advisable therefore to determine a number of factors usually found useful in working with unstable resin compounds. A number of samples of hops of known quality and origin were examined for moisture, soft resins (Milwaukee method); hard resin (CS_2 extract); acid value (from Neumann test); Koettsdorfer value (mg. KOH required to saponify 1.0 g. hops); Ester value; volatile acids, or Reichert-Meissl value; and the iodine absorption value. The methods employed were the standard ones in general use, and were only modified to suit these special conditions, without, however, changing the methods.

A careful study of the figures will reveal that they are constant with the quality, and worthy of consideration.

While it is necessary, in order to draw definite conclusions, that we have figures from a large number of analyses it is apparent from even the test of these few samples that a constant variation exists between these figures of hops of a good and of a poor quality.

The claim has been made that the volatile oil of hops remains in the beer to some extent, and that it exerts a powerful influence on the aroma of the beverage. In order to gather some data on this topic, I made a series of experiments by boiling various samples of hop oil in water and in wort. As was to be expected, a great part of the hop oil passed off with the steam. The remaining liquid was then extracted with ether, and the ether evaporated at a low temperature. In this way I found that 10% of the hop oil is still present after two hours boiling, while 5 to 8% is present after four hours boiling. As hops contain (Chapman) about 0.5% essential oil, by giving hops in the proportion of

1:750, we would have about 0.0000665 per cent. essential oil in the wort. This quantity, though small, would be important if still capable of flavoring the beer, for, as we know, only minute quantities are needed to produce an effect on the olfactory nerves. My experiments, however, showed that the residue of the ether extract, which of course is nothing but a hop oil remaining after two hours resp. four hours boiling, has no aroma whatever, but behaves in a way similar to resin. It thus appears that the aromatic oil is volatilized by boiling, while a portion is converted in a non-volatile non-aromatic substance, which will not impart any aroma to beer.

Origin	No.	Quality Crop.	Moisture %	Soft resins %	Hard resin %	Total resins %	Acid val. mg KOH per 1.0 g	Koetts- dofer value	Ester value	Volatile acids	Iodine value % iodine absorbed
Oregon	1	Good 1911	9 78	18 80	1 97	20.77	29.1	189.8	160.7	15 32	42 41
Oregon	2	Poor 1911	11 01	10 34	7.11	17.45	24.4	151.2	126.8	15 06	37.46
California	3	Good 1911	10.64	20 00	1.45	21.45	30.0	207 2	177.2	16.00	41.91
California	4	Poor 1911	9.58	14.71	2.18	16.89	23.6	91 8	68.2	13.40	31.37
Washington	5	Good 1911	11 08	18.89	1.36	20.25	28 3	161 8	133 5	15 20	35.05
Washington	6	Poor 1911	8 98	14.28	4.25	18.53	25 9	119 8	93.9	14.34	33.78
New York	7	Good 1911	10 21	13.77	1.25	15.02	21 2	106.4	85 2	13.62	31.75
New York	8	Poor 1911	9.72	10.79	3.66	14.45	20.2	95.2	75 0	12 88	29.21
Bohemian	9	Good 1911	8.74	15 08	1.00	16 08	22.5	181.8	159.3	14 90	29.46
Bohemian	10	Poor 1910	9.07	14 07	3 19	17 26	24.5	161 8	137 3	14 45	28.95

Conclusion

In conclusion I wish to state that, although the usual methods of hop analysis (soft resins and hard resin) are adequate for their

rapid estimation of the brewing value of the hops, it becomes necessary to determine other factors when the accurate comparison of hops of different quality is wanted.   Among the data collected in my recent experiments, I find that the determination of the saponification or Koettsdorfer value and of the Ester value give useful information as to the relative value of hops.   The iodine absorption number also gives the experimenter an idea of the proportion of unsaturated compounds, and the corresponding ease with which the resinous bodies can undergo changes.

PRACTICAL OBSERVATIONS AND STUDIES OF ALBUMEN

TURBIDITIES IN BEER, CAUSED BY TIN AND IRON

BY GUSTAV L. GOOB

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Turbidities in beer caused by minute particles of colloidal albumen are very often a severe tribulation to the brewer. Although not very commonly met with in draught beer, they most frequently appear within a short time in bottle beers which are marketed in pasteurized condition. The causes of such colloidal albumen precipitations are many, and not always is the brewer himself able to locate the exact seat or seats of the difficulty. The consulting brewers' chemist, to whom the puzzling problem is then submitted, usually does not receive an explicit history and all facts and details of the case, so as to allow him to make the proper diagnosis and form the correct deductions, and thus locate definitely the condition or conditions at fault.

In the instance of albumen turbidities brought about by the effect of metal on the beer, a proper diagonsis of the case usually is the quickest solution of the entire problem, because as soon as it is definitely known that the albumen precipitation is caused by metal, the source of the defective metallic contact can easily be located. Under average brewery conditions, only two metals are met with, which may detrimentally affect the quality of the beer. These are *tin* and *iron*.

TIN

Bare or unprotected tin is the most active as far as the formation of an albumen haziness is concerned, and its action is very rapid. Usually the effect of tin on the beer manifests itself within a few hours in pronounced cases and within 24 to 72 hours in very slight ones. Aggravated cases are easily detected, *first*,

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by the characteristic appearance of the beer, *secondly*, by a microscopical examination, and *thirdly*, by a chemical analysis. All three should be made very carefully, though the chemical analysis only gives satisfactory results in very pronounced cases. To the experienced practitioner a pronounced so-called tin turbidity in beer becomes immediately evident by its characteristic greenish-gray opalescent appearance, which is radically different in this respect from any other albumen turbidity.

The difficult instances with which the brewers' chemist comes in contact, are those where only a very slight, sometimes almost insignificant albumen haziness in the beer was caused by tin. In such cases, a chemical analysis is out of question, as a definite chemical reaction of the tin cannot be obtained, even when large quantities of the beer are tested. The appearance of the beer is no longer so characteristic as in such instances where there is a pronounced tin turbidity, but it is more like that of a beer showing an ordinary albumen haziness. There is still, however, a distinct tendency towards the greenish-gray opalescence, which is readily apparent to the analyst or brewer who has had experience in difficulties of this kind. The microscopical examination allows for a good indication of such slight tin haziness, inasmuch as the precipitated albumen particles are so small that they cannot be seen by means of a magnification of 400-500 diameters, whereas the particles from an ordinary albumen precipitation can easily be seen. Since none of the ordinary examinations conclusively show the cause for the slight albumen haziness, an investigation in the brewery is the proper step in order to obtain the final proof and at the same time locate the source of the trouble.

In most cases, nowadays, the tin turbidity manifests itself when the metal employed for tinning the surfaces with which the beer comes in contact, is impure. The corrosion usually occurs in small spots, which plainly make their appearance on the metal. The employment of block tin, which must be properly applied, precludes any detrimental effect on the beer, providing the metal surfaces are properly coated with shellac varnish. As rapidly as this coating of shellac wears off, it is replaced by a protective film of the so-called " beerstone," which, however,

will not form over defective spots caused by either impure tin or imperfect tinning.

According to Mr. Chapman, President of the Brewing Institute, England, one-tenth grain of metallic tin per gallon of beer will produce a very marked haziness. This is equivalent to 1.7 milligrams of tin per liter of beer or about 0.2 grm. per barrel. Based upon my own observations in practice, it is impossible to state with accuracy how minute a quantity of tin may have a detrimental effect on clear, viz., filtered beer, inasmuch as the amount contained in the beer showing only a slight haziness due to the metal cannot be definitely determined by chemical means. An instance of tin turbidity which I observed recently was caused by introducing 4 newly tinned filter cells into a 22-cell filter. The beer immediately after filtration was perfectly brilliant in appearance, but after standing at cellar temperature (about 3° C.) for 24 hours, a very faint haziness was perceptible. This increased slightly within the next 48 hours, so as to become sufficiently distinct as to give rise to complaints from the trade. The beer at no time showed a pronounced cloudiness. The slight haziness was of the characteristic greenish-gray opalescence, and reached its maximum within 72 hours. After that time, the beer did not change in appearance, whether warmed to room temperature or packed into chipped ice for 24 hours. The microscopical examination showed that the finely divided albumen particles could not be seen by means of a magnifying power of 400-500 diameters, but first by employing one of 800-1,000. There was absolutely no reaction of tin when the beer was examined chemically.

An investigation of the filter showed that each of the four new cells had corroded at about a dozen or more places, none of which was greater in area than about 0.50 square centimeter and most of them less than 0.25 square centimeter. The metal was only very slightly roughened at the corroded spots, and a conservative estimate of the amount of tin dissolved by the beer from all four of the cells could safely be placed at less than 1 gram. Inasmuch as about 500 barrels of beer had been passed through the filter, the quantity of tin dissolved (based upon 1 gram) amounted to less than 0.018 milligram per liter. Even this figure undoubtedly

is considerably too high and the minimum quantity of metallic tin which can produce a perceptible haziness in beer is very much smaller. That this albumen haziness really was caused by tin was proven conclusively by the fact that as soon as the four newly tinned cells were replaced by old ones, the filtered beer remained perfectly brilliant and showed no manifestations of haziness.

It is surprising that the brewers have adhered to the employment of tin for so long a time, considering that such extremely small quantities will affect the brilliancy of the beer, especially if it is placed on the market in pasteurized condition. With the advent of aluminum and the knowledge of properly working this metal, it is only a matter of time before all conduits and surfaces with which the beer or wort comes in contact will be made thereof. There is absolutely no danger of any effect on beer when the aluminum is of high purity, viz: 99.5-100% pure. The main question which still remains unanswered is the one regarding the life of the metal for the different purposes in the brewery.

IRON

Iron and steel vessels have been employed in the brewery for many years, and in only few instances have serious disturbances occurred, which actually could be traced back to the action of this metal. Under normal conditions, the wort at the time of pitching with yeast will contain at the utmost only a faint trace of iron, as determined by the potassium sulpho-cyanide method, and this amount can remain in the beer without danger, inasmuch as it is insufficient to affect the quality of the finished product detrimentally, whether it is placed on the market as draught or pasteurized bottle beer. In those instances, which have come under my personal observation, where disturbances were produced in the beer by the action of soluble iron, it was invariably found that the metal was first taken up by the beer after the fermentation period and it did not manifest its presence during the storage, clarifying and finishing stages; in fact the beer acted entirely normal during these periods of production. In the finished product, the presence of iron shows itself in a characteristic way, depending on whether

the beer is marketed as draught or pasteurized bottle beer. The draught beer containing iron will show it by the behavior of the foam of the beer when drawn into the glass, whereas the bottle beer will easily become hazy or cloudy due to albumen precipitation after it has been bottled about 2 weeks or longer. In both instances the oxygen of the air is an important factor, inasmuch as the iron in the beer at the time of racking or bottling is present in the form of a ferrous salt and while in that state is inactive. But as soon as oxygen is introduced, it is changed to the ferric salt, which immediately forms an insoluble reddish-brown albumen combination.

In the case of draught beer, which was drawn into the glass, only the foam shows the effect of the iron, because it is directly exposed to the air, whereas the beer itself is not affected. The characteristic behavior of the foam is that it gradually forms very coarse bubbles, and draws away from the sides of the glass forming a " floating island " of foam, which is similar in consistency to the beaten froth of white of egg and slightly but distinctly reddish-brown in color on the exterior. The beer, however, is not made hazy or turbid nor is the taste affected to a noticeable extent, even if a considerable amount of soluble iron is present.

The brilliancy of bottled beer containing iron will not be impaired during the pasteurizing operations, but it will be more prone to albumen haziness if placed in chipped ice for 24 hours. When poured into the glass, however, it shows the same characteristic behavior of the foam as is the case in draught beer. After the beer has been bottled and pasteurized for about 2 weeks, the action of the iron becomes noticeable. Augmented by the small quantity of oxygen of the air contained in the empty space in the neck of the bottle, the insoluble ferric albumen combination deposits in the form of a sediment, or causes the beer to become hazy. This albumen precipitation continues as long as any iron is in solution or any oxygen is present. During this time, the beer not alone becomes cloudy, but it also darkens in color and changes radically in taste and flavor.

Repeated observations of beers containing iron have demonstrated these changes, and the greater the amount of soluble iron present and the larger the amount of air in the neck of the bottle,

the sooner does the albumen precipitation set in. It has been found frequently that in bottles of the same batch of iron-containing beer, some showed only a very slight sediment whereas in other bottles the sediment was very voluminous. In such cases, the beer having the very slight sediment was filled into the bottle in such a way that a slight foaming occurred during the filling operations, and in consequence the air was almost completely displaced and the space filled with carbonic acid gas. A very slight amount of air will always be introduced when putting the crown cork on the bottle, but it is too insignificant for practical consideration. The bottles first mentioned, viz., the ones showing the very slight sediment, contained only very little oxygen which could act upon the ferrous iron and oxidize it to the ferric salt and as a result a correspondingly slight quantity of albumen was acted upon so as to make it insoluble.

Frequent tests of iron-containing beers in Pasteurized condition have demonstrated that the iron-albumen precipitation constituting the sediment gives a very pronounced reaction of iron, whereas the clear beer above the sediment showed only a faint trace. This usually occurred in poorly filled bottles where a large air space was contained in the neck.

In order to verify these findings chemically, the addition of a chemical having a reduced action, for instance, meta-bisulphite of potash (K. N. S.), was made to a clear beer giving a distinct reaction of iron. When poured into the glass shortly after treatment, the treated beer did not show the pronounced discoloration and " lumping " of the foam the way the untreated beer did. The Pasteurized beer which was treated did not have a sediment until after about 2 months had elapsed, whereas the untreated beer became hazy within 3 weeks.

It is therefore evident that small quantites of iron dissolved in beer are present in the form of a ferrous salt and are inactive until oxidized to a ferric salt. They then combine with the albumen, and in the case of draught beer cause the foam to become discolored and " lumpy." A Pasteurized bottle beer on the other hand suffers greatly in keeping qualities, inasmuch as the beer becomes hazy or a sediment forms therein, and it loses the desired clean, beery taste and flavor, providing there is sufficient oxygen

present in the empty space in the neck of the bottle so that the oxidation can take place. If none is present or only a trace of it, there is practically no danger of a detrimental effect of small amounts of ferrous iron on the stability of the beer. As simple as this seems, it nevertheless is almost impossible to exclude the air, inasmuch as there will always be the action on the foam of the beer as soon as it is poured into the glass. It, however, is well worth the effort to remove the air from the neck of the bottle in the case of bottle beer, on account of the improvement in stability and preservation of taste.

The places where the iron can be dissolved by the beer are numerous, and space only allows mentioning a few of the more important ones. The majority of brewers do not seem to realize the importance of protecting their product from direct contact with iron surfaces during the storage, clarifying, and subsequent operations. Iron rods, manhole doors, and other fittings frequently are in bad condition, for instance, the iron may be " spongy" or may have become rusty in spots. Iron pipes through which beer passes or of which enclosed beer coolers are constructed, often are in a similar state. In the case of glass enamelled steel tanks, the enamel may have been chipped off in places, and thereby the bare metal spots exposed so that the beer comes in direct contact with and dissolves iron, especially during the chip cask period. The employment of plain steel fermenters, storage or clarifying tanks, which are to be coated with a shellac varnish or other suitable enamel is extremely hazardous, especially when producing bottle beer. As soon as the metal surfaces become rough in spots, the varnish or enamel coating no longer adheres properly, and the beer will dissolve some of the iron. When in this poor condition, tanks must be scraped, rubbed with emery paper, re-heated, and re-coated, in order that the difficulty may be overcome. The installation of such tanks is to be strongly deprecated.

Cases of iron turbidity have also been traced to the employment of water containing iron for washing the filtermass, the iron precipitating on the fibre of the mass during the process and becoming dissolved as the beer is being filtered. In another instance, iron found its way into the beer through drippings from the pipe conveying the air from the air pressure pump. This air must be

suitably trapped before entering the cask containing the beer which is to be displaced through air pressure.

As stated in the concluding remarks regarding tin turbidities, the introduction of an inert metal like aluminum, for constructing brewery vessels and apparatus, will do away with the dangers from metal turbidities, to which the beer is exposed nowadays. Glass enamelled steel tanks are equally satisfactory, but the precaution must be observed that the enamel is not chipped off or otherwise injured so as to expose the beer to the bare metal. It is well worth the greater expenditure necessary to have all conditions as near to perfection as possible, thus insuring the greater safety.

LA STÉRILISATION DES VINS

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Contrairement à ce qui a lieu pour la transformation du jus de raisin en vin-opération qui exige le concours de ferments organisés-le vieillissement normal du vin fait, s'accomplit par voie purement chimique. Peut-êrte, à la vérité, les phénomènes chimiques du vieillissement dépendent-ils, dans une certaine mesure, de la présence de certaines diastases ou de certains agents catalytiques encore indéterminés (traces de manganèse, par exemple). Mais il est établi depuis longtemps que la " bonification " d'un vin ne s'accomplira sûrement que si ce vin est complétement exempt des micro-organismes apportés par la grappe ou introduits accidentellement au cours de la fermentation.

C'est donc à l'élimination ou à la destruction de ces micro-organismes que tendent tous les modes de traitement préconisés pour la conservation des vins. Les plus usuels sont le collage, ou mieux une succession de collages et de soutirages, et la pasteurisation ou chauffage à 60-65° C. On a aussi obtenu de bons résultats par la congélation ou tout au moins par un refroidissement intense. Je ne parle que pour mémoire des procédés chimiques, auxquels j'estime qu'on ne devrait avoir recours que si les procédés physiques échouent ou ne peuvent pas être appliqués par suite de circonstances particulières.

Or, les divers traitements que je viens de mentionner ont un désavantage commun, qui est de modifier plus ou moins la composition chimique du vin. Les collages et soutirages répétés abaissent notablement le poids des matières extractives, atténuent la couleur, et de plus, occasionnent une perte de liquide souvent onéreuse. Ils exigent aussi beaucoup de temps, des manipulations longues et fastidieuses.

La pasteurisation, de beaucoup supérieure, influe très peu sur la composition générale du vin, mais elle a le défaut de lui communiquer un goût de " cuit " peu agréable. On a prétendu,

il est vrai, que le consomma teur s'y accoutume; cela ne veut pas dire qu'il en soit heureux, et il l'en est si peu que tous les perfectionnements récents apportés aux pasteurisateurs ont principalement pour objet d'éviter cette altération du bouquet.   J'admets que la chose ait une importance médiocre pour les vins grossiers, de consommation courante.   Il n'en va pas de même pour les vins de qualité, dont le producteur et le negociant doivent veiller à sauvegarder la finesse.

Quant à la congélation, elle n'agit en réalité que grâce à la précipitation de certaines substances extractives, qui entraînent mécaniquement les germes organisés suspendus au sein du liquide.   Elle doit, au demeurant, comme la pasteurisation, être suivie d'un repos assez long et d'un soutirage.

Enfin, ce qui manque à ces procédés, c'est une garantie réelle d'efficacité.   La pasteurisation, par exemple, n'est certainement efficace que si le vin a subi pendant un certain temps l'action d'une température relativement élevée.   Pour éviter ce goût de cuit dont j'ai parlé, on abaisse, le plus possible et la température du chauffage et sa durée.   Or, dans ces conditions " limites " on perd évidement toute certitude.   Ce qui sera suffisant dans tel cas sera insuffisant dans tel autre; chaque vin devra être étudié comme un cas d'espèce, et la moindre anomalie, insensible ou inaperçue, pourra avoir une répercussion fâcheuse sur les effets ultérieurs du traitement.

Le vieillissement normal ne sera donc assuré que par une véritable *stérilisation* du vin fait.   On ne saurait songer à y employer la chaleur, car le vin ne peut supporter qu'une température modérée.   Mais nous disposons pour cela d'un moyen dont l'efficacité a été amplement démontrée à l'égard d'autres liquides: c'est la filtration sur paroi poreuse, sur bougie.

Une difficulté se présente ici.   N'importe quelle bougie filtrante, à pores suffisamment ténus, pourra stériliser un vin. Mais il est essentiel que la matière du filtre n'ait aucune réaction chimique sur les substances dissoutes dans le liquide.   Ainsi, certaines bougies que l'on voulut destiner à cette application, et qui renfermaient un excès de chaux, avaient l'inconvenient de saturer en partie les acides du vin (quelquefois dans la proportion de

25%), et cette saturation partielle avait pour conséquence un virage désavantageux de la couleur: il fallut renoncer à leur emploi.

Pareil inconvénient ne se produit pas, si l'on fait usage de filtres neutres, indifférents aux agents chimiques. Tel est la cas du Filtre Mallié, en silicate de magnésie. M. Magnier de la Source, d'une part, M. M. Bordas et Durand-Fardel, d'autre part, ont constaté, il y a plusieurs années, que le passage du vin à travers ce filtre n'en modifie pas les caractéristiques essentielles et que sa couleur n'est aucunement altérée. De plus, le filtre retient tous les ferments de maladie: mycorderma vini et acéti, filaments de la tourne, bâtonnets de l'amertume, etc.

Ayant eu récemment à analyser un vin blanc de Touraine "remonté" par sucrage et qui était encore en pleine fermentation, et désirant en conserver une partie dans l'état même où je l'avais reçu, en vue d'un contrôle éventuel, j'ai eu l'idée de le filtrer sur une bougie Mallié. Je constatai que la fermentation était ainsi complètement arrêtée. Tandis que le vinnon filtré (qui m'avait été remis presque limpide) ne tarda pas à devenir fort trouble, à abandonner un dépôt abondant de ferment et à dégager de l'acide carbonique, le vin filtré, au contraire, demeurait parfaitement limpide, même dans un flacon à-demi plein et à la température du laboratoire. Ce résultat, du plus haut intérêt, montre qu'il est possible d'arrêter la fermentation au point voulu, en une seule opération et sans introduction d'anti-ferment. Il m'a semblé utile de poursuivre l'étude de cette question et premièrement, de rechercher quelles modifications les différents modes de traitement du vin apportent dans sa composition. A cet effet, je me suis procuré un vin (d'un petit crû bordelais) n'ayant encore subi d'autre travail que le soutirage sur lie, et je l'ai soumis aux opérations suivantes:

(a) Filtration sur bougie Mallie;

(b) Collage, à la dose de 6 blancs d'oeufs pour 200 litres de vin;

(c) Pasteurisation à 65° C. avec réfrigération immédiate;

(d) Congélation, et dégel lent à la température ambiante.

Avant de procéder à l'analyse, le vin provenant des opérations *b, c* et *d*, fut filtré sur papier.

Voici les résultats de mes déterminations:

	Non traité	Filtré sur bougie	Collé	Pasteuri-sé	Congelé
Degré alcoolique	9°.6	9°6	9°6	9°6	9°6
Extrait dans le vide	24.62	24.42	24.00	24.56	23.72
Acide tartrique total	2.24	2.22	1.76	2.23	1.44
Tannin et mat. colorante	4.96	4.98	4.73	4.98	4.96
Acidité totale, en SO_4H_2	3.53	3.53	3.43	3.53	3.33

On voit que la filtration sur bougie Mallié, de même que la pasteurisation, n'atteint aucun des principaux éléments du vin. Pour tout dire, j'ai constaté dans le vin filtré une légère diminution de la gomme (ou de ce qu'on désigne sous ce mon) dosée par le procédé Reboul: 2g. 07 après filtration, au lieu de 2g. 38 avant. Mais on sait combien cette détermination est incertaine; ce que j'annonce ici debra donc être confirmé. La couleur du vin, loin d'être affaiblie, acquiert au contraire plus d'éclat, conséquence d'une limpidité plus grande; la nuance, d'ailleurs, n'est pas modifiée, c'est-à-dire qu'il n'y a aucun *virage* de la couleur. De même, la saveur est parfaitement conservée.

Le tableau ci-dessus donne en outre une idée des modifications provoquées par le collage et la congélation. Elles sont assez faibles, certes, mais cependant sensibles. Et l'on conviendra qu'il vaut mieux généralement employer, pour la conservation du vin, un procédé qui en respecte intégralement la composition.

J'ajouterai qu'ayant mis en observation, dans des flacons en vidange, une partie du vin non filtré et du vin filtré, j'ai vu bientôt la premier se recouvrir d'un voile épais de mycoderma vini et laisser déposer un sédiment coloré abondant, alors que le second, dans les mêmes conditions, conservait sa limpidité et ne présentait aucune végétation superficielle.

Sur les vins ainsi traités, je me propose de faire une nouvelle analyse après un vieillissement d'une année, au moins. Dès maintenant je puis dire que la filtration sur bougie en silicate de magnésie n'entrave en aucune façon les phénomènes chimiques auxquels est dû le développement du bouquet. Les filtres Mallié,

en effet, sont utilisés depuis de longues années déjà dans un grand nombre de chais, en Bourgogne notamment, et les résultats pratiques obtenus furent toujours des plus satisfaissants.

En résumé, la stérilisation à froid, par filtration, apparaît donc comme le procédé de choix non seulement pour le traitement des vins malades, mais encore pour la conservation des vins sains destinés à voyager ou à vieillir en cave. Elle se recommande tout particulièrement lorsqu'il s'agit de vins fins, dont le bouquet délicat et la couleur ne résistent pas à l'application d'une température de 60° C. (minimum nécessaire pour la pasteurisation).

Il va de soi que d'autres boissons peuvent aussi être traitées de la sorte. Le cidre et la bière, par exemple, gagnent beaucoup à ce traitement. J'ai eu entre les mains un échantillon de cidre, datant de plusieurs années, conservé en bouteilles après filtration sur bougies Mallié: il était parfaitement limpide, sans trace de fermentation secondaire.

UEBER DIE KONIDIENBILDUNGSFAEHIGKEIT EINIGER VARIETAETEN DES ASPERGILLUS ORYZAE

Von Genitsu Kita

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Was die Beziehung zwischen der Fruktifikation und der Naehrstoffe anbelangt, ist schon einiges bekannt. Nach Backmann[1] verhindert erhoehte Konzentration Kochsalzes die Sporenbildung von Mortierella, foerdert aber auf festen Naehrboden die Entstehung von Gemmen. Raciborski[2] zeigte, dass Saprolegnia in 10% Gelatine nicht mehr Sporen bildet, wobei dahingestellt bleibt, wieweit hier die Konzentration mitwirkt. Von den Naehrstoffen hat Bittersalz einen grossen Einfluss; nach Coupier und Friedel[3] biltet Asp. versicolor blaurosafarbige Konidien anstatt der normalen gruenfarbigen in einer magnesium freien Raulin schen Naehrloesung.

In meiner Untersuchung ueber die Varietaeten des Asp. oryzae fand ich einige Arten, die ausser physiologischen Eigenschaften sich in Bezug auf Farbe und Bildungsfaehigkeit der Konidien ganz besonders verhalten. Eine Art (A10) z. B. bilden keine Konidien auf Plattenkultur mit Kojigelatine (Kojidekokt von 10° Ba. + 10% Gelatine), und hat ein ganz besonderes Aussehen. Aber eine solche Art hat auch Konidienbildungsfaehigkeit und nach einer Versuchsreiche bestaetigte ich, dass der Wasser gehalt dabei Einfluss hat. Zustande des Wachstums unter verschiedenen Bedingungen sind unten skizziert.

(1) Zusatz von 5 bezw. 10 grm MgSO aq. in 100 cc. Kojigelatine (10%) oder Kojiagar (2%) hat keinen bemerkenswerten Einfluss auf das Wachsen und die Konidienbildung.

Die Pilzernte sind unten angegeben.

[1] Jahrb. wiss. Bat., 1899, Bd. 34, S. 279.

[2] Flor, 1896, Bd. 82, S. 107.

[3] Comptes rend. de l'Ac., 1904, 138, 1118.

Kojigelatinekultur.   15 Tage bei 20-23° C.

MgSO₄- Menge	Arten					
	A10	K3g	K1	S	K7w	K5
0	1,2480	0,8522	0,8592	0,8364	1,1060	0,8548
5	1,1590	0,8390	0,8618	0,9973	1,1642	0,8724
10	0,9990	0,9388	0,9920	0,8300	1,1490	0,7560

A10 (aus dem Aichi-Gebiet) . . . . . . nur weisse Mycelien.

K3gu. K1 (aus dem Kumamoto-Gebiet) . . gelbe Mycelien.

S (aus Shozushima). . . . . Mycelien etwas wattenfoermig, Konidienbilding schwach).

K7w (aus dem Kumamoto-Gebiet) . . . . Konidien gebildet aber schwach.

K5 (aus dem Kumamoto-Gebiet) . . . . . . Konidienbildung sehr gut, als normale Art in Vergleich genommen.

(2)   Einfluss der Temperatur. Sie wurden auf Kojigelatine ausgesaet und in zwei verschiedener Temperaturen (20° und 30° C.) gezuechtet. Das Wachsen blieb sich gleich mit demselben Aussehen von einer bestimmten Art. Die Pilzertnte waren wie folgt.

Kulturdauer.   10 Tage.

Kulturtemp.	Arten				
	A10	K3g	K1	K7w	K5
20 C	0,3880	0,2840	0,3282	0,5116	0,3228
30 C	0,7798	0,2974	0,6263	0,6178	0,3478

Von oben sieht mann, dass die Pilzernte je nach der Art und Züchtungsweise sehr verschieden ist.

(3)   Die Zuechtung in Kojidekokt unterscheidet sich je nach der Varietaeten. Die komidien-Farbe der folgenden Arten war von gerb bis gelbgruen der Reihenfolge nach.

K1, K3g, K7w, S, A10, K5 (gruen).

(4) Auf Kleie mit vielem Wasser (10 T. KLEIE· 35 T. Wasser) waren Farbe und Bildungsfaehigkeit der Konidien bei einigen Arten verschieden von den normalen Arten.

(5) Auf Lederextraktgelatine (10%) wachsen sie ueppig mit gelben Konidien und unterscheiden sich nicht besonders.

(6) AUF der duennen Kojigelatineschicht bilden die Arten, die auf dicker Schicht derselben keine Konidien order abnormale bilden, auch gute, gruene Konidien. Aus dieser Tatsache schloss ich, dass der Wassergehalt des Naehrbodens eine wichitige Rolle bei der Konidienbildung spielt und versuchte deshalb den Einfluss der grossen Menge Wasser auf Brot.

(7) Ein Brotstueckchen lies ich in Erlenmayerkolben mit Wasser schwimmen und nach Sterilisation wurden fuenf Arten in einen betreffenden Kolben ausgesaet. Wachstumszustand war verschieden mit wenigen Konidien je nach den Varietaeten, waehrend K5 (normale Art) mit gruenen Konidien bedeckt war. Dies bestaetigt meine obere Schlussfolgerung.

(8) In frueheren Versuchen brauchte ich den Naehrboden mit 10% iger Gelatine und derselbe verfluessigte sich waehrend der Kultur bei 20° bezw. 30° C. Erfolg mit groesserer Menge Gelatine und $MgSO_4$ (15% Gelatine, 10% $MgSO_4$) wurde bei diesem Versuch probiert. Nach zehn taegiger Kultur bei 20° C. wurde der Unterschied bei einigen Arten bemerkt, weil sie nur wenige Konidien gebildet hatten. Aber nach 14 Tagen waren sie auch mit vielen Konidien bedeckt und der Unterschied war nicht bedeutend, weil sie alle von gelbblauer Farbe war.

Wachstumszustand in Naehroboden ohne $MgSO_4$ war verschieden je nach der Varietaeten wie bei 10% iger Kojigelatine.

Zusammenfassung

(1) In meiner Untersuchung ueber die Varietaeten des Asp. oryzaefandich einige Arten, die ausser physiologischen Eigenschaften sich in Bezug auf Farbe und Bildungsfaehigkeit der Konidien ganz besonders verhalten.

(2) Eine solchen Varietaeten haben auch normale Konidienbildungsfaehigkeit, z. B. auf Brot und noch auf duenner Schicht der Kojigelatine bilden sie normale gruenen Konidien.

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(3)   Nach einer Versuchsreihe bestaetigte ich, dass der Wasser-
gehalt eine Rolle bei der Konidienbildung einiger Varietaeten
spielt.

(4)   Dies ist ein neues Beispiel, dass der Wassergehalt auf die
Fruktifikation eines Pilzes einen grossen Einfluss hat. Es gibt
einige Pilzarten, die keine Sporen bilden, sondern nur hefeartige
Zellen abschnueren, wenn sie in die Naehrlosung getaucht werden.
Das ist aber ein ganz besonderer Fall. In diesem Falle wuerde
der Wassergehalt fuer die Varietaeten so guestig sein, dass sie
Konidien nicht bilden, um ihre Art zu bewahren. Der Mangel an
Wasser im Gegensatz dazu fuer das Wachsen ungeuenstig und
foerdert die Konidienbildung.

HAUPTHEFE DER SOJAMAISCHE

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Bei Sojabereitung spielt die Alkoholgärung neben diastatischer, proteolytischer und Säure produzierender Einwirkung eine wichtige Rolle. Der aus Stärke gewonnene Zucker wird in Alkohol vergoren, der sich weiter in Ester verwandelt, um einen Bestandteil des Sojaaroma zu bilden. Unter den Hefen des Sojamaisches isolierte Dr. Saito[1] eine neue Art, Saccharomyces Soja als einen Hauptgärungserreger und bemerkte, dass sie von Sacch. Saké, Yabe ganz abweicht, während die beiden Genussmittel von Koji mit demselben Pilz, Asp. oryzae, bereitet werden. Im Jahre 1909-1910 habe ich verschiedene Maische von den berühmten Orten für Sojabereitung gesammelt und Hefe darin isoliert. Für Isolierung der Hefen impfte ich Sojamaisch in Salz Kojidekokt. Nach einer Woche, als die Entwicklung der Hefen üppig war, verdünnte ich das Dekokt in sterilisiertem Wasser und kulturierte in üblicher Weise auf die Platten von Kojigelatine mit 10% Kochsalz. Mit abermaliger Plattenkultur stellte ich Reinkultur nach der Art von Lindners Tröpfchenkultur an. Nach den Resultat enthalten die Maische, die sich in der Gärung befinden oder einmal stark gegoren haben, eine eigentümliche Hefeart, die in den meisten Punkten die gleichen Eigenschaften wie Sacch. Soja hat, aber sie bildet nicht Endosporen und gehört deshalb nicht zu Saccharomyces, sondern zu Torulaart. Sacch. Soja, die nach Saito die wichtigste Hefeart des Sojamaisches ist, wurde nie gefunden.

1. Allgemeine Eigenschaften

Die Zellen sind meist rund, manchmal elliptisch mit dicker Wand, die leicht sichtbar unter dem Mikroscop ist. Plasma wel-

[1] Centralbl. f. Bakt., 2. Abt., Bd. 17, 104, 152.

lenförmig, Vakuol wird seltens bemerkt. 4.5-8 μ. gross in Kojide-kokt.

Kolonie auf Kojidekokt-Gelatine-Agar ist rund oder stern-förmig, gelb gefärbt, erhöht sich in der Mitte hügelförmig, glatt am Rande.

Riesenkolonie auf demselben Nährboden ist gelb, in der Mitte eingesunken, ihre Oberfläche körnig, wellenförmig am Rande. Strichkultur ist nass, gelb, körnig an der Oberfläche und wellen-förmig am Rande.

In Kojidekokt ohne oder mit 10% Kochsalz entwickelt siesich üppig, sinkt nider und bildet einen Hefering mit einer Ausnahme, die im gesalzenen Kojidekokt flockig suspendiert. In Hängtrop-fenkultur nach Lindner bildet sie anfänglich Sprossverband, aber zergliedert sich alsbald je nach der Entwicklung. Sie gärt Glukose, Maltose, aber nicht Galaktose, Sukrose, Laktose, Raffinose, Arabinose.

Sacch. Soja gärt desgleichen Glukose und Maltose, aber nicht Sukrose, wie bei meiner Art. Nach Saito enthält Sacch. Soja Invertin als ein Endoenzym. Meine Art wiess auch die Ein-wirkung des Invertin nach Zerreiben der Zellen auf, aber das Dasein des Zymogen Invertin anzunehmen ist rational, weil die Gegenwart des Endoinvertin keine Erörterung der Ungär-barkeit der Sukrose zulässt. Die scheinbare Gärkraft beträgt 70-75° und wird bei 35° C. stark herabgedrückt mit Ausnahme einer Art. Alle wachsen und gären gut bei 28° C.

Die junge Hefe auf dem Gipsblocke bildet keine Endosporen, und die alte im Hefering auch nicht, während Sacch. Soja im Hefering nach Saito diese Fähigkeit hat.

Vergleich meiner Art mit Sacch. Soja usw. Wie oben gezeigt, unterscheidet sich meine Art von Sacch. Soja durch Gärfähigkeit von Galaktose, Sporenbildungsfähigkeit und Form der Riesen-kolonie. Von Affinität mit anderen Torula Arten finde ich keine mit denselben Eigenschaften, aber die Beschreibung von einigen Arten ist unvollkommen, um sie zu vergleichen und es benötigt noch weitere Versuche mit den bekannten Arten anzustellen.

(2)   Gärkraft in verschiedenen Lösungen.

.   (a)   In Kojidekokt mit Kochsalz.
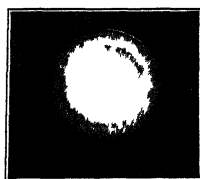
½ NAT. GR

Dass die Sojahefe starke Garkraft in gesalzener Losung hat, kann man nach ihrer Abstammung vermuten. Der folgende Versuchy wurde unternommen, um den Einfluss derselben zu vermitteln. 50 cc. Kojidekokt (10° Ba.) mit 2 cc. Hefebrei wurden im Kolben mit Garventil mit Schwefelsaure bei 25° C. vergoren, und die Menge der verlorenen Kohlensaure bestimmt.

Menge CO₂ verloren in	Salz zugesetzt in grm.				
	0.0	0 5	2 5	5 0	10.0
1 Tage	——	——	——	——	——
2	0,1769	0,1790	0,1850	0,1774	0,0290
3	0,1964	0,2102	0,2502	0,3342	0,0240
4	0,3058	0,2443	0,2792	0,2566	0,0918
5	——	——	——	——	——
6	0,5715	0,4530	0,4516	0,4148	0,2004
7	0,0820	0,1006	0,1438	0,1037	0,0814
8	0,0304	0,1538	0,0592	0,0554	0,0652
Summe	1,3630	1,3409	1,3690	1,3421	0,4868

Während die Gärkraft der Brennereihefe R. II. bei Gegenwart von etwa 5% igem Salz beträchtlich herabgedrückt wird, hat eine noch grössere Menge keinen störenden Einfluss auf Sojahefe, sondern wirkt zu Anfang fördernd.

    (b) In Kojidekokt ohne Salz.

Um die Garkraft zu vergleichen, wurde Saccharomyces cerevisiae angewandt. Die Versuchsmethode war ganz dieselbe wie bei (a), die gleiche Hefezahl wurde ausgesät.

CO₂ Menge verloren in	Kojidekokt von			
	10° Ba.		20° Ba.	
	Sacch. cerev.	Sojahefe.	Sacch. cerev.	Sojahefe.
1 Tage	0,0642	0,0320	0,0482	0,0327
2	0,9600	0,1400	0,1312	0,1968
3	0,2099	0,2566	1,2748	0,2162
4	——	——	——	——
5	0,0981	0,7100	1,1520	0,5498
6	0,0243	0,1212	——	——
7	——	——	0,3354	0,6942
8	0,0215	0,0988	——	——
10			0,0430	0,3311
Summe	1,3779	1,3586	2,9744	2,0070

Obwohl die Gärkraft der Sojahefe in Vergleich mit der Bierhefe zu Anfang sehr schwach ist, so erhöht sich die Kraft nach etwa vier Tagen, so dass der Unterschied nach 8 Tagen nicht so gross ist.

(c) Vergleich der Gärkraft der Sojahefe von verschiedener Abstammung in Kojidekokt (10° Ba.) mit 10% igem Kochsalz.

CO₂ Menge verloren in	Hefeart					
	1 (aus Sakaı)	2 (″)	3 (″)	4 (Schizuoka)	5 (Noda)	6 (Tatsuno)
1	0,0442	0,0560	0,0369	0,0636	0,0778	0,0690
2	0,2890	0,2952	0,3232	0,2934	0,3510	0,2998
3	0,2090	0,2210	0,2490	0,2042	0,2430	0,2910
4	0,2278	0,2372	0,2304	0,2088	0,2200	0,2282
5	0,2152	0,2276	0,1816	0,1792	0,2080	0,1742
6	0,1240	0,1122	0,1010	0,1086	0,1360	0,0876
7	0,0798	0,0760	0,0760	0,0922	0,1000	0,0510
8	0,0552	0,0472	0,0416	0,0544	0,0652	0,0293
Summe	1,2542	1,2724	1,2397	1,2044	1,2010	1,2301

Der Gärungsvorgang der Hefe unterscheidet sich nicht beson-
ders durch Abstammung. Das Resultat der Bestimmung der
Hefezahl war auch das gleich.

      (d)   In Würze mit Alkohol.

Jedem 50 cc. der Würze (10° Ba.) wurden verschieden grosse
Menge Alkohol (95 vol. %) zugesetzt und diese mit 2 cc. Hefebrei
vergoren.

CO$_2$ Menge verloren in	Alkohol-Menge zugesetzt in cc.						
	0 0	0 5	1 5	2 5	3 5	5.0	7 5
1 Tage	0,1130	0,1270	0,1210	0,0647	0,0796	0,0560	0,0440
2	0,2314	0,2670	0.2580	0,1050	0,0348	0,1060	0,0088
3	0,2842	0,3152	0,3010	0,1884	0,0568	0,0110	0,0098
4	0,3604	0,2819	0,2220	0,1134	0,0943	0,0068	0,0062
5							
6	0,4408	0,2943	0,3192	0,2605	0,0570	0,0212	0,0212
Summe	1,4295	1,2854	1,1212	0,7320	0,3225	0,1100	0,0900

Eine kleine Menge Alkohol fördert die Gärung zu Anfang,
aber nicht zum Schluss. Obwohl die Hefe gegen Salz gut wie-
dersteht, wird ihre Kraft durch etwa 10% Alkohol herebgedrückt.

      (3)   Über Gewöhnung der Hefe in Salzlösung.

Das Verhalten der Sojahefe in Salzlösung ist bemerkenswert.
Wie sich andern Hefe z.B. Sacch. cerevisiae durch Gewöhnung
verhalt, und wie die Sojahefe im Gegensatz dazu nach der
wiederholten Kultur in Würze ohne Salz ihre Eigenschaft ändert,
sind interesante Fragen.

Einige Versuche über die erste Frage waren ohne Erfolg.
Die wiederholte Kultur der Sojahefe in Würze ohne Salz ver-
ringerte nicht ihre Gärkraft in Würze mit Salz, aber die Kraft
in Würze ohne Salz wurde durch die wiederholte Kultur in
Salzlösung verstärkt.

Versuch: Nach zehnmal wiederholter Kultur verkleinerte
sich die Hefe in gesalzener Würze, aber nahm mehr an Zahl zu
als die in Würze ohne Salz.

150 cc. Würze (10° Ba.) wurden mit 3 cc. Hefebrei vergoren.

CO_2 Menge verloren in	Salzmenge zugesetzt in Grm			
	Mit der in gesalzener Würze gezuchteten Hefe		Mit der in Würze ohne Salz gezuchteten Hefe	
	(1) 15	(2) 0	(3) 15	(4) 0
1 Tage	0 1790	0,1373	0,0900	0,1464
2	0,8460	0,6785	0,7504	0,6074
3	0,7678	1,5634	0,7932	0,8764
4	0 7562	1,2718	0,8044	0,7770
5	0,5554	0,6408	0 6144	0,6228
6	—	—	—	—
7	0,5646	0,5706	0,6098	0,8970
8	0,1090	0,1686	0,1124	0,2972
10	0,1184	0,2030	0,1284	0,2710
12	0,0774	0,1616	0,0592	0,1700
14	0,0354	0,0990	0,0182	0,0740
Summe	3,8082	5,5452	3,9924	4,7392
Alkoholmenge	4 980	6,08	5,25	5,80
Zuckermenge als Maltose	3.31	0,63	2,51	1,07

In diesem Beispiel ist die Gärung (1) schlechter als (3), aber bei dem anderen Beispiel mit Kojidekokt ist sie umgekehrt. Jedenfalls ist der Unterschied nicht so gross, dass man die Veränderung der Eigenschaft vermuten kann.

Aus diesen und früheren Versuchen kann man leicht bemerken, dass die Gegenwart des Salzes die Gärung nur zu Anfang reizt, aber zum Schluss schlechten Erfolg hat. Gegen unsere Vermutung hat die Gewöhnung der Sojahefe in gesalzener Würze keinen wirksamen Einfluss auf die Garung in gesalzener Würze, und es ist eine ganz besondere Erscheinung von Anpassung der Zellen an Gift. Wenn die Eigenschaft der Verstarkung der Gärkraft in süsser Würze durch die wiederholte Kultur in gesalzener Würze allgemein wäre, verspräche es einen Vorteil im Brennereibetrieb, aber mein Versuch mit R. II. war negativ.

(4)   Bedeutung der Alkoholgärung bei Sojabereitung.

Wie ich oben wiederholte, spielt die Gärung eine wichtige Rolle in der Sojabereitung, und das Sojaaroma wird teilweise ihrer Einwirkung verdankt. Beim Auflösen der Bohnen wurde

Kohlensäurebildung auch imstande sein, ihr Gewebe zu lockern, so dass die enzymatische Einwirkung erleichtert wird, obwohl die Hefe selbst keine scheinbare proteolytische Einwirkung darbietet (Kita; J. S. Chem. Ind., Tokio, XIV, 123). Aber in Wirklichkeit hängt Aroma und Geschmack des Soja hauptsächlich von Proteinsubstanz der Sojabohnen ab. Eine grosser Teil des gebildeten Alkohols geht verloren im Verlauf der längeren Bereitungsperiode. Die Bestimmung des Alkohols in Soja nach der Permanganatmethode gibt nur einige Prozent an. Nach Vermutung auf dieser Seite stellte ich einige Versuche von Veränderung der Mengeverhältnisse der Maische und von geeigneter Anwendung der Hefe an, woüber ich an anderen Stelle berichten will.

ZUSAMMENFASSUNG

Ich habe von verschiedenen Sojamaischen eine wichitige Hefe, die zu der Torulaart gehört, gefunden. Diese ist meist rund geformt mit dicker Wand, Grösse 4, 5-8, 0μ. Die Riesenkolonie auf der Kojigelatine agar ist in der Mitte eingesunken, und ihre Oberfläche körnig. In Kojidekokt mit oder ohne Kochsalz gedeiht sie üppig, sinkt nieder und formt nur einen Hefering. Sie gärt Glukose und Maltose, aber nicht Sukrose, Galaktose, Laktose. Raffinose und Arabinose. Der Zellbrei enthält Invertase, aber dieses Enzym wild vielleicht gleich nach dem Zerbrechen der Hefezellen gebildet, weil die lebende Hefe keine Sukrose gärende Kraft hat. Die scheinbare Gärkraft betragt 70° und gärt energisch bei 28° C., aber sehr schwach bei 40° C. Nicht auf jede Weise werden die Endosporen gebildet, und sie gehört zu der Torulaart.

Die Eigenschaften der Hefe sind wie bei Sacch. Soja, Saito, die gleichen mit Ausnahme der Gärfähigkeit für Galaktose, Sporenbildungsfähigkeit und Form der Riesenkolonie.

Sacch. Soja wurde nie gefunden.

Die Gärkraft wird durch 10% Kochsalz niemals beeinflusst, sondern zu Anfang der Gärung gefördert, aber wird durch etwa 10% Alkohol herabgedruckt.

Die wiederholte Kultur der Hefe in Kojidekokt mit Kochsalz vermehrt die Hefezahl im Einheitsraum und verringert die Grösse.

Die wiederholte Kultur der Hefe in Wurze ohne Salz verringert nicht ihre Gärkraft in gesalzener Würze, aber die Gärkraft in Würze ohne Salz wurde durch die wiederholte Kultur in Salzlösung verstärkt.

Bei der Sojabereitung spielt die Alkoholgärung eine wichitige Rolle, aber sie verlangt einige Verbesserung, um in geeigneter Weise angewandt zu werden.

INFLUENCE DE LA PRESSION SUR LA FERMENTATION ALCOOLIQUE

Par MM. L. Lindet et L. Ammann

Paris, France

Le Dr. P. Regnard a montré que la levure, comprimée brusquement à 600 atmosphères, ne perd pas ses propriétés fermentatives (Comptes-rendus de l'Académie des Sciences, 1884. T.98.P.745) Mais ces conditions sont tellement éloignées de celles où la levure évolue d'ordinaire, et se prêtent si mal à des mesures précises, qu'il nous a paru intéressant d'étudier, à des limites moins élevées, l'influence de la pression sur la fermentation alcoolique. Cette étude avait été commencée par l'un de nous pour des pressions n'allant pas au delà d'une atmosphère au-dessus de la pression ordinaire. (Bin. Soc. chimique, 1889, p. 195).

I.—Nous introduisons un moût de touraillons, ensemencé de levure, dans une bouteille à Champagne, dont le col, rodé, reçoit un tube de verre, qui s'élargit au niveau du goulot de la bouteille, et s'applique exactement par rodage sur celui-ci; l'extrémité inférieure du tube descend à quelques millimétres du fond de la bouteille; l'extrémité supérieure est reliée, au moyen de forts caoutchoucs à des tubes de verre épais et de petit diamètre intérieur.

Au lieu d'une pression constante dès le début, nous avons préféré réaliser une pression progressive au moyen de l'acide carbonique produit par la fermentation même; nous reviendrons sur ce point qui peut être discuté.—Nous ne pouvions demander au moût contenu dans la bouteille de marquer, le long du tube manométrique, la pression à laquelle il était à chaque instant soumis, non seulement parce que le moût aurait ainsi laissé échapper son acide carbonique, mais également parce que, désirant atteindre une pression aussi forte que notre appareil pouvait la supporter, il eut fallu prolonger les tubes à une hauteur

excessive, et c'est ainsi que nous avons été amenés à placer une couche de mercure dans le fond des bouteilles.

Cette couche de mercure pouvait-elle avoir une influence sur l'étude du phénomène? Des expériences préliminaires nous avaient montré que le mercure, dans ces conditions, retarde d'environ 24 H le départ de la fermentation, mais ne diminue pas le pouvoir ferment de la levure. D'ailleurs, nous n'avons pas à tenir compte de la présence du mercure; car à coté de la bouteille sous pression, se trouvait une bouteille témoin, simplement bouchée avec un tampon de coton, et contenant du mercure et la même quantité de moût ensemencée. Ces bouteilles ne pouvaient pas être stérilisées par la chaleur; elles étaient lavées avec une solution de bichlorure de mercure puis à l'eau stérilisée.

Les courbes que nous avons tracées, en relevant chaque jour la hauteur atteinte par le mercure dans le tube manométrique, montrent que la fermentation a été aussi régulière que si elle avait été conduite à la pression normale.

Quand la dose de sucre ne dépasse pas sensiblement 3% du moût, on voit, après une période pendant laquelle l'acide carbonique se dissout dans le moût, le mercure s'élever régulièrement, en fonction du temps, jusqu'à une hauteur qui a varié de 1 m40, à 1m 80; à partir de ce moment l'élévation du mercure est plus lente; la courbe tend à devenir horizontale, et la hauteur du mercure atteint son maximum vers 2 m. et 2 m.20. Nous avons pu obtenir des pressions supérieures, en ajoutant aux moûts plus de 3% de sucre; la courbe s'est elevée encore régulièrement; mais les joints qui reliaient les tubes barométriques ont alors laissé échapper du mercure avant que la courbe ait pris son horizontalité.

D'une façon générale, la fermentation a été deux ou trois fois plus lente dans les bouteilles sous pression que dans les témoins, ce qui n'a pas lieu de surprendre, puisque, dans les premières, l'air ne se renouvelait pas. Pour la même raison, la levure s'y est reproduite en moindre quantité, mais la quantité d'alcool a été la même, dans le cas où la fermentation a pu s'achever; dans le cas contraire, la dose de sucre restant montre que le moût sous pression aurait produit autant d'alcool que l'autre, si sa fermentation avait pu s'achever.

Exp. I

| | | Fermentation
terminée
après: | Pour 100 de moût | |
			Alcool en cc.	Levure en gr.
Mout sucré à 3,2%	{ sans pression { avec pression	6 jours 13 jours	1,85 1,83	0 218 0.122

Exp. II

		Alcool % du mout, en cc.	Alcool correspondant au sucre restant dans le mout	Alcool total en cc.
Mout sucré à 6%	{ Sans pression terminée { après 5 jours { Avec pression non termi- née après 11 jours	5 50 4,65	0,00 0 87	5 50 5 52

Nous ne méconnaissons pas que l'appareil ci-dessus décrit ne puisse être critiqué. On peut en effet supposer un appareil clos, où on enverrait dès le début une pression d'air, et qui porterait une soupape équilibrée permettant à l'acide carbonique de se dégager sous pression constante; l'atmosphère intérieure eut pu également être constamment renouvelée par un envoi d'air sous pression; mais ces appareils sont difficiles à réaliser, si l'on veut qu'ils supportent pendant plusieurs jours une forte pression gazeuse; en outre, nous risquions de mettre en contact de la levure une quantité d'air supérieure à celle que le témoin recevait, et nous exposer à une critique contraire à celle qui peut être faite vis à vis de notre appareil, où l'air est plutôt en défaut.

D'ailleurs, si l'on peut démontrer que, pour une même quantité d'air, l'excès de pression n'a pas d'influence sur le développement en nombre des globules de levure, on ne pourra attribuer

qu'au défaut d'aération le faible pouvoir reproducteur des globules sous pression, et par conséquent le ralentissement de la fermentation.   Dans ce but, nous avons réparti, à l'intérieur de deux tubes à essais, une même quantité de bouillon gélatiné et sucré, préalablement ensemencé d'une même quantité de levure; l'un de ces tubes a été déposé dans une des branches d'un gros tube en U, que l'on a ensuite scellé à la lampe; l'autre branche était reliée à un tube manométrique par lequel on a coulé du mercure, jusqu'à ce que l'air du tube en U ait été comprimé à 3 atm., 3, par une colonne de mercure de 2 m.50; d'autre part, le second tube ensemencé, introduit sous une cloche de même capacité que la branche de compression du tube en U, reposant sur le mercure, servait de témoin.   A aucun moment de leur développement, les colonies de l'un et de l'autre tube ne se sont montrées différentes, ni sous le rapport du nombre, ni sous ce lui de leur dimension diamétrale.   La levure se développe donc, sous une pression de 2 m.50, et en présence de la même quantité d'air, avec la même rapidité qu'à la pression atmosphérique.

On peut donc conclure de ces expériences que la pression de 3 atmosphères ne gène pas la prolifération de la levure, que la fermentation suit une marche identique, quelle que soit la pression que supporte la levure, au moins jusqu'à 2 m.80 de mercure, et produit la même quantité d'alcool; que c'est à la diminution, d'aération qu'il convient d'attribuer, dans les expériences précédentes, la diminution du poids de levure formée et le ralentissement de la fermentation alcoolique.

DOES THE HARD RESIN OF THE HOP IMPEDE THE SOLVENCY OF THE SOFT RESIN IN PETROLIC ETHER AND BEER WORT?

By Emil H. Naatz

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The tendency at present in the brewing trade is to save as much hops as possible. In the light of modern investigations, this tendency is both warranted and just. In practically every phase of beer manufacture, modern methods have not only replaced older ones, but have brought about a saving of material, as well as improved the quality of the product. Considering the success in other parts, the lack of it in the use of hops is all the more plain by the contrast. In the majority of cases, improved methods in practice have followed successful investigations in the laboratory. It is due to the uncertain data gathered in laboratory investigations on hops, that greater uniformity does not exist between laboratory and practical hop valuation, and that the promises from chemical tests have not all been realized in the brewery.

It is not my purpose to enter into any discussion on the valuation of hops or the relative value of the methods employed to judge such article, nor to attempt any explanation of the complex changes that take place in the extraction of the bitter substances by the wort, and further in the beer. On the contrary, it is my object to draw your attention to some mechanical influences, which, though perhaps slight and apparently overlooked by most observers, may have considerable influence in the extraction of the valuable constituents of hops.

There are a number of substances in the hops which are of value to the brewer. As is generally conceded to-day, the important constituents (from a brewer's standpoint) are all of a resinous character. These substances are only found in certain parts of the hop strobile, in that portion generally known as hop flour or lupulin. The lupulin,which may also be compared to a

glandular scale, consists mainly of these resins, with thin retaining walls or layers of cellulose material; also mineral matter; while carbohydrate and proteid substances are present in small amount.

Numerous investigators have classed these resinous bodies as hop oil, soft resins, hard resin, and wax or fatty matter. The amount of hop oil is small, and, while it may be important to some extent, it does not require special attention here. The total soft resins as separated by recognized methods, form a clear, amber colored, semifluid mass, easily soluble in ether, petrolic ether, carbon bisulphide, methyl alcohol, and also to a great extent in water. The hard resin is a much darker substance, thick or wax-like. It is soluble in ether, carbon bisulphide, methyl alcohol, very sparingly soluble in petrolic ether and in water. The wax is yellowish in color, solid, and soluble in ether, petrolic ether, and carbon bisulphide, but practically insoluble in methyl alcohol or in water.

It is understood that during the curing and storing of hops and lupulin, a gradual oxidizing process takes place, whereby the soft resins are partly converted into hard resin. As will be noted from the structure of the lupulin, this change can only take place along the surface of the gland, whereby the original mass of oily, semifluid soft resins is surrounded by a layer of hard resin. Whether oxygen penetrates the hard resin coat or whether the latter transmits the element by a process of repeated oxidation and reduction is not known. It is a fact that this process usually is slow, but may be hastened by rupture of the wall, thus exposing a fresh surface. In a similar way, those solvents of soft resins, which do not also dissolve the hard resin, are influenced.

There are various influences which will modify the results by augmenting or retarding the extractive power of the solvent. In determining the resins in hops, the sample is usually extracted with ether, using petrolic ether (having a boiling point below 50° C.) for soft resins, and ether or carbon bisulphide for hard resin. To determine the actual temperatures of the solvent while the extraction was going on, I placed thermometers in both the boiling flask and the Soxhlet.

Temperatures of various solvents in different parts of the Soxhlet apparatus, during extraction:

TABLE No. I

	Ether		Carbon Disulphide		Methyl alcohol		Petrolic Ether boiling moderately		Petrolic Ether boiling violently	
	Lower flask on water bath	Extraction chamber (Soxhlet)	Lower flask on water bath	Extraction chamber (Soxhlet)	Lower flask on water bath	Extraction chamber (Soxhlet)	Lower flask on water bath	Extraction chamber (Soxhlet)	Lower flask on water bath	Extraction chamber (Soxhlet)
Max.	35.5	34.0	45.5	43.0	67.0	52.0	40.70	30.5	43.0	32.5
Min.	34.5	27.5	45.0	24.5	65.0	42.0	38.5	29.0	41.0	31.5
Av.	34.9	32.1	45.4	39.6	66.0	45.9	40.2	29.9	42.7	32.1

(Temperatures are degrees centigrade.)

Where C. Lintner's or O. Neumann's method is used, the temperature of the ether naturally corresponds to that in the flask marked " lower " in the above table.

I also determined the melting point of these resins. No attempt was made to separate the " soft resins " from each other, but the mass obtained by methyl alcohol from the petrolic ether extract was used.

TABLE II

Melting and solidifying point of Hop Resins:

(Degree centigrade)

Resins	Melting Point	Solidifying Point
*Soft resins (a + b)	33.0–35.5°	30.5°
Hard Resin (y)	66.5–75.0°	60.0°
Wax	63.0°	62.0°

*In a few cases the mixture of soft resins even melted at a temperature of 23.0° C.

The temperature of boiling petrolic ether is considerably lower than the melting point of the hard resin. If the boiling point of petrolic ether approaches the melting point of the soft resin, the petrolic ether extract of the hops is increased, as is shown by the experiments of G. Feuerstein.

During recent years, I have analyzed a large number of hops and lupulin samples of different origin and quality. Practically every known method has been tried. Formerly the entire strobiles were extracted with petrolic ether and ether. The petrolic ether extract varied greatly, even if hops were extracted more than 8 hours; the ether extract was fairly constant. It is not probable that the petrolic ether would penetrate the strobile less thoroughly than ordinary ether. When I began to grind the hops in a small meat chopper, the petrolic ether extract increased, and comparative analysis showed that ground hops gave a higher percentage of soft resins than whole hops extracted in a similar way. The microscopical examination of these hops, ground in the chopping machine, showed that much of the lupulin (though not all), was ruptured—caused by the pressure and grinding motion. I now modified the grinding by using the finest knife of the machine; after leaving the machine, the hops were ground with sand in a mortar. Practically *all* the lupulin in these samples was ruptured. These ground samples of hops and lupulin were then extracted, while a corresponding series of whole hops and lupulin were extracted in a similar way. In the latter case, the strobiles were cut into pieces, but care was taken not to injure the glands. The lupulin samples were also mixed with sand, but were not ground. The results are shown in table No. 3.

TABLE III

Origin and Quality	Moisture	Whole Hops			Crushed and Ground Hops		
		Petrol Ether Extract	CS₂ Extract	Total Resins Ext'd	Petrol Ether Ext'd	CS₂ Extract	Total Resins Extracted
	%	%	%	%	%	%	%
Bavarian medium 1911	8.74	11.95	4.14	16.09	15.08	1.40	16.48
Bohemian medium 1910	9.07	7.17	8.69	15.86	14.58	2.25	16.83
Bohemian medium '10	8.76	6.22	9.52	15.74	14.93	1.80	16.73
New York fair '11	10.21	6.22	7.06	13.28	13.45	1.25	14.70
New York good '11	8.64	6.79	6.69	13.48	12.83	1.35	14.18
New York medium-old	8.63	6.95	9.04	15.99	13.25	2 78	16.03
New York inferior	10.04	7.49	6.51	14.00	10.65	4.15	14.70
Oregon choice '11	9.78	11.73	7.27	19.00	20.80	1.03	21.83
Oregon choice '11	10.26	11.59	5.97	17.56	17.35	1.04	18.39
Oregon-old inferior	7.41	7.03	9.97	17.00	15.20	1.95	17.15
Oregon choice '11	6.35	14.19	6.41	20.60	18.24	2.01	20.25
Oregon inferior '11	9.42	11.61	5.74	17.35	12.36	4.90	17.26
California choice '11	10.03	12.32	6.80	19.12	18.30	1.70	20.00
California choice '11	10.64	13.90	6.97	20.87	20.00	1.45	21.45
Lupulin Bav. fresh. light col.	5.08	30.26	32.74	63.00	38.80	25.63	64.43
Lupulin Bav. old. hardened dark colored	5.10	12.48	44.52	57.00	26.60	30.85	57.45

The figures in the above table are the average for several determinations. When extracting the thoroughly ground hops, the figures obtained agreed well, while those of the whole hops showed some variations for the same sample. As is also obvious from the table, the difference in the amount of soft resins is greater in old or inferior grade samples where the layer of hard resin is thicker and more difficult to penetrate.

The experiments were repeated in some of the samples, using distilled water and beer wort (with a gravity of 1.0485). The samples were boiled in whole and crushed condition. The liquid was then cooled, filtered, and the resin extracted with ether and petrolic ether in separatory funnels. The results are given in table No. 4.

TABLE IV

	Time of boiling	Hops				Lupulin			
		Fresh		Old		Fresh		Old	
		whole	Crushed	whole	Crushed	whole	Crushed	whole	Crushed
Ether extract of 1000 cc water	¼ hr	60	125	40	100	242	580	94	483
	2 hr	100	400	95	385	340	664	240	520
Petrol ether extract of 1000 cc water	¼ hr	12	55	18	98	60	207	40	180
	2 hr.	35	84	29	116	200	410	100	340

(All figures are milligrams)

The results with wort are similar to those with water, though slightly lower. In the above experiment the hops were added in the proportion of 1:500. The lupulin was in the same proportion; consequently will give higher results on account of more resin being present.

I believe that these results indicate that the hard resin impedes the rapid solution of the soft resins. In laboratory tests of hops, where low boiling point solvents are used, this effect is very marked. In such hops where the hard resin layer has reached some thickness, this resin may prevent the complete solution of soft resins in the usual time allowed for extractions. That the retarding influence is not due to the cellular walls, is shown by the fact that the influence is felt more with old deteriorated hops than fresh ones, and it is more probable that the resinous bodies undergo greater changes than any of the other substances in the strobile. When hops are boiled with wort, the difference is not near as great, except when the boiling period is very short. The high temperature of the wort will melt the hard resin, and thus remove the insoluble layer around the soft resins. It thus becomes possible that solvents of varying boiling point will not give uniform results (except when they are also solvents of hard resin), and that laboratory results, as far as soft resin determinations are concerned, do not always agree with those of practical tests in boiling wort. By grinding hops so that all the lupulin is ruptured, this difficulty should be removed.

THE MATERIALS USED IN THE MANUFACTURE OF FILTER-MASS

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Until comparatively recently the use of the filter and filtering media was limited largely to water purification and a very small number of industries. To-day the filter plays a significant part in the arts and manufactures, and occupies a place in the various industries the value of which is hard to overestimate. This sudden appreciation of the value of filtration is the consequence of modern methods of manufacture characterized by the substitution of mechanical methods for manual labor, together with an enormous output.

Processes based upon sedimentation, had to be replaced of necessity, by methods which would require less time and work with greater certainty and uniformity. This was largely the state of affairs in the brewing industry. Not only did the introduction of the filter into the brewery practically do away with the long periods of storage on chips, which limited the output and consequently represented financial loss, but it enabled the brewer to work with a type of yeast which, though possessing poor clarifying powers, was found desirable for other reasons. Furthermore filtration of beer insures greater stability in the finished product, and this is, unquestionably, the best argument in its favor.

In view of this it appears strange how little has been published on this subject. With the exception of an occasional article appearing at long intervals in one or other of the trade or technical journals, the scientific literature on the subject, which ought to be of vital interest to the brewer, remains very fragmentary. The examination and valuation of filter mass has likewise, for some unknown reason, received very little attention by the scientific stations. It seems that there is to-day very little uniformity as to the methods of valuation by different stations, both in the

United States and abroad, and that the system of analysis now in vogue is inadequate. Not only does it appear desirable to eliminate as far as possible the subjective element now present in the valuation of filtermass, but it further would be well to supplement the present microscopical examination in every instance by a trustworthy and practical microchemical one, and likewise, to amplify the chemical analysis by a number of additional determinations, and if possible establish a systematic method of valuation, largely objective, which would be applicable in all cases and could, therefore, be adopted by the scientific stations everywhere.

As this paper was nearing completion, my attention was called in June to an article by Dr. H. Zykes.[1] I read this article with a divided feeling. On the one hand, I was very glad to see that a man of practical experience, like Dr. Zykes, had taken up the matter of the analysis of filtering materials for beer, realizing no doubt the importance of the subject for the practical brewer. On the other hand, I was very sorry that I was not aware any sooner of the work that was being done by Dr. Zyke, as such intelligence would have meant a saving of considerable time and would have enabled me to supplement, rather than to repeat, the work already done by him. As it is, I feel confident that Dr. Zykes has treated the subject thoroughly, and glad to see that my results are in good agreement with his. His work needs little amplification, and it is hoped that, together with present, it may form a basis for more extensive research on the materials used in the filtration of beer.

The word " filtermass " as it is used to-day conveys to our mind the conception of a white fibrous mass, consisting of cellulose in the form of cotton or wood fibres, sometimes also containing small admixtures of other plant fibres such as linen, hemp, jute and ramie. This, however, was not always the case. On the contrary the materials used for the filtration of beer have been subject to frequent modification and change, with the result that to-day the manufacturer is more limited in the selection of his raw materials than he has ever been before.

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[1] " Zur Ueberpruefung von Bierfilterstoffen," Z. ges. Brauw., 1912, **35**, 205-10, 222-25.

Likewise, the question as to whether filter paper or filter pulp is more to be desired as a medium for beer filtration, was an open one until comparatively recently.

Experience had taught that owing to its feltlike character a very thin layer composed of filter papers gave results which could be equalled only by using a thick cake of cellulose. Paper had the further advantage that beer remained in contact with it for a shorter time than with pulp. Furthermore, the filter losses were minimized, and the time required for packing the filter was shorter. If the efficiency of such a filter fell off to a large extent, owing to the accumulation of particles on the surface of the filtering medium, it was necessary only to remove the top layers of paper and to replace them by new papers and the original efficiency would again be restored. With filtermass the washing, sterilizing, and packing, requires considerable time.

The reason why, in spite of all these advantages possessed by the paper filter, the pulp filter has now been practically universally adopted, is due to the lower cost of pulp filtration. Owing to the fact that in paper filters the used papers cannot be used again, the cost of operation is much higher. The pulp filter, furthermore, permits of a more rapid filtration.

But the pulp filter is not faultless, as yet, and has many disadvantages. E. Ludwig finds,[1] as does also Windish,[2] and Franke,[3] that modern filters remove too much from the beer, having as a result a product of poorer foam retaining capacity, and at the same time imparting to it an unpleasant foreign flavor. This he attributes to the substitution of dense cakes of solid pulp for a mass of lose pulp such as was formerly used. As a consequence of this tight packing of the filter modern beer filtration becomes more or less a process of surface filtration, like that customary in the laboratory, the surface of the cakes of pulp rapidly becoming coated with a layer of impurities, through which the beer has to be forced under enormous pressure. Furthermore, as these impurities are by far more easily soluble in beer under high pressure than at moderate pressure, they are, as the process

[1] Wochenschr. Brau., **21**, 214-5.
[2] Wochenschr. Brau., **21**, 93-5.
[3] Wochenschr. Brau., **21**, 327.

of filtration proceeds, gradually redissolved imparting to the beer the characteristic flavor complained of by some people in filtered beer. E. Ludwig[1] suggests a system of filtration in which the impurities would be removed in a series of progressive operations under low pressure, thereby avoiding the accumulation of impurities on the outer surface of the medium. This principle has been applied in an American filter which has already been introduced in many breweries.

It is also quite likely that this end could be attained, most easily and effectively, by combining the centrifuge and the filter, as has also been suggested by C. Angermann.[2] If this were to be done, however, it would be necessary to carbonate the beer artificially after the same has passed the filter since the centrifugal force, removes the greater portion of the gas from solution.

There is on the market now a machine of this clarifier and filter type, which, as far as the brilliancy of the filtered beer, and the removal of yeast cells and bacteria is concerned, can be surpassed only by filters which employ a filtering medium made of Infusorial Earth. From a number of experimental tests which were conducted for me by the manufacturers, I am convinced that the principle upon which the machine is built is the correct one, unfortunately, however, the capacity is very limited and in comparison the cost of installation and operation so prohibitive as to render the machine impossible for beer filtration on a large scale. Another advantage is that not pulp but only a few sheets of filter paper are required, the centrifugal force always keeping the surface free from an accumulation of impurities. Judging from the favor it has found in other industries dependent upon filtration, it is not unlikely that the manufacturers may at some time in the near future, succeed in modifying their machine in a manner which will overcome these difficulties.

A type of beer filter entirely different in principle from the pulp and paper filters, has been placed on the market by an Eastern manufacturer. In this filter a porous plate or plates consisting of a material of the nature of Infusorial Earth is used as a

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[1]Wochenschr Brau, 21, 214-5

[2]Wochenschr Brau, 28, 1911, 604-7.

filtering medium.   The diatomous structure of this material makes it practically impossible for yeast cells, and likewise bacteria, to pass through, and the claim is, therefore, made that provided no infection enters the beer after it leaves the filter, the same does not require pasteurization.   This filter is already in use in a number of breweries in this Country and as I understand gives entire satisfaction.

Another novel form of filter is now manufactured and sold in England.   The apparatus depends upon finely divided Kieselguhr spread in a uniform layer on filter paper and cloth as a filtering medium, and in type of construction resembles a filter press, with round chambers mounted horizontally between base plate and cap plate.   The Kieselguhr is claimed to be a chemically inert and tasteless filtering agent, giving a brilliant filtrate in far larger volume and at one half the expense and trouble as compared with pulp filters.   At present it is hard to predict just what the success of this apparatus will be, as it has not been on the market very long.

As to the essential qualities which a good filtering material for the purpose of beer filtration should possess, the following points may be safely laid down:

    1.   It should impart no taste, odor or color to the beer.
    2.   It should give a brilliant filtrate,
        a. Without high pressure,
        b. Without requiring a very heavy layer of filtering material.
    3.   It should remove yeast cells and bacteria without injuring the palatefulness and foam holding capacity of the beer.
    4.   It should be easy to clean and sterilize.

To accomplish this, the fibres or other materials to be used in the manufacture of the filtering medium should be,

    1.   Free from oily, fatty, alkaline, acid, or resinous substances, and other substances, which may be soluble in water or 4% alcohol.
    2.   It should be free from mechanical wood pulp. (lignin.)
    3.   If fibres are used, these should be long and uniform in diameter, and not too thick.

  4.   There should be no knots, or agglomerates of fibres not easily separated by agitation with water.

  5.   If asbestos is used it should not be alkaline.

The raw material now largely used in the manufacture of high grade cotton filtermass consists of new white cotton cuttings from textile mills. This is first sorted, the seams and hems are opened out, and is then delivered to a machine technically known as " rag duster " and consisting of a hollow cylindrical or conical drum having an external covering of coarse wire cloth, which rotates inside a wooden box. The shaft is provided with projecting spikes, so that the rags are violently agitated in their passage through the machine. The dirt and other impurities fall through the wire unto the floor of the room, while the rags are discharged from the lower end of the drum. These are next separated into smaller parts by a " rag cutter," and transferred to a spherical digester, technically termed " rag boiler," and capable of holding approximately 500 pounds in one charge. Here they are boiled with milk of lime for about 5 hours under a pressure of from 5 to 6 atmospheres. The high temperature, together with the action of the chemical, removes the fatty, resinous and starchy matter from the material.

After the rags have been sufficiently boiled they are washed in the " Hollander " and then transferred to a " dripping chamber " which serves the purpose of removing the excess water and any heavy particles that may be present, by sedimentation. Next they are transferred to a machine known as the " breaking engine," where they are further washed and reduced to a condition of fibrous lint, called " half-stuff." This half-stuff is next centrifuged to remove the water, and then introduced into a machine known as the " Hollander " beating engine, which serves the purpose of further separating the material into the ultimate fibres, which are so essential for good filtration.

If impure material is used, it will further be necessary to bleach the pulp so obtained with acid, and subsequently wash it to perfect neutrality with filtered water. After this operation the material, mixed up with water, is sometimes made to pass through an apparatus consisting of a box with a bottom of perforated

plates with slits $\frac{1}{16}$ inch wide, which move up and down and retain even the smallest knots.

I am informed by one of the largest German manufacturers of filtermass, that for the manufacture of one pound of filter mass about 360 gallons of filtered water are required.

The materials entering into filtermass to-day can be classified into:

A. *Vegetable Fibres:* Cotton, linen, ramie, hemp, and jute.
B. *Wood Fibres:* Cellulose in the form of mechanically and chemically prepared wood pulp.
C. *Mineral Fibres:* Asbestos.

It should be borne in mind that a filtermass consisting of a variety of different fibres is more likely to change, as regards efficiency of filtration, after a repeated use than a mass composed of one kind of fibres only.   This is due to the fact that some fibres, owing to their nature, deteriorate more rapidly than others, especially when they are treated with alkali or oxidizing agents, and thereby the relative proportion of the fibres present in the mass is changed.

Vegetable Fibres: Zykes in his recent paper[1] has given a description of the vegetable fibres, both as regards their character and microscopical appearance, so that I shall limit myself to a table which I have compiled to show the chemical composition of the five vegetable fibres which are likely to be present in filtermass.[2]

	Flax %	Cotton %	Hemp %	Jute %	Ramie %
Cellulose	81.99	91.35	77.13	63.76	66.22
Wax	2.37	0.40	0.55	0.38	0.59
Aqueous Extract	3.62	0.50	3.45	1.00	10.34
Moisture (hygroscopic)	8.60	7.00	8.80	9.86	10.15
Ash	0.70	0.12	0.82	0.68	5.63
Pectous Substances	2.72	——	9.25	24.32	12.70

[1] Z. ges. Brauw., **35**, 205-10.

[2] Compiled from figures given in Dr. H. Mueller, " Pflanzenfaser."

From this table it is easily seen that cotton is the ideal fibre for the manufacture of filtermass, at least as regards chemical composition. It is over 90% pure cellulose, contains no pectous substances, very small per cent. of ash, practically no water soluble substances, and only 0.4% of wax and similar ether-soluble substances.

Ramie is a very valuable fibre, partly due to the lack of an efficient process for properly decorticating the fibre from the rest of the plant, and has therefore, so far, been limited to the textile industry. It usually enters into filter-mass as a waste material from such sources.

Wood Fibres: Wood pulp is of two kinds, mechanical and chemical. *Mechanical pulp* is made by forcing a large stick of wood against a revolving sandstone, or emery wheel, over which a jet of water plays continuously. Hence the German word " Holzschliff " for mechanical wood pulp. The water passes through and a layer of pulp adheres to the cylinders and is delivered on to an endless blanket, by means of which it is transported to a pair of squeeze rolls which render it compact. Mechanical wood pulp is contaminated with lignin and resinous matters which turn brown on exposure to air. It is, therefore, undesirable for filtermass, furthermore, the fibres possess very little strength, gradually lose their fibrous character, and do not mat together well. *Chemical pulp*, may be either soda, sulphate, or sulphite pulp depending upon the process of preparation. In the course of any of these processes the non-cellulose matters of the wood, (lignin, resins, etc.,) which consist largely of organic acids, are decomposed or combine with the soda, and consequently the alkali is nearly all neutralized during the process.

The caustic soda has a direct action on the cellulose itself, especially when the pressure is high, hence some of the fibre is dissolved, and all of it slightly weakened. The wood produced is very soft, and although possessed of a dark color is easily bleached. H. Will[1] is of the opinion that wood cellulose, (chemical pulp) is better adapted for beer filtration than cotton because it is coarse and more easily separated, and consequently, easier to wash.

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[1] Z ges. Brauw , **19**, 618.

With the addition of a small percentage of asbestos a very satisfactory mass is obtained.

Mineral Fibres: Asbestos. K. Windisch[1] who analysed a number of samples of asbestos intended for the filtration of wines, found that all of them contained substances of an alkaline nature, which were soluble in water and capable of modifying the acidity and flavor of the wine.[2] It is, therefore, natural to expect that the addition of asbestos of this character to pulp or mass used for the filtration of beer is likely, if not certain, to influence the beer in a similar manner. Some of the samples examined by Windish gave a strong coloration when digested with cold distilled water containing phenolphthalein, while all of the samples reacted alkaline after heating. I have digested ten different samples of filter mass with cold water and found that one gave a decided coloration with the above indicator. As the mass contained about 3-5 per cent. of asbestos, the alkalinity may have been due to this source.

Windish further found that when asbestos was digested with warm water for two days, soluble substances of an alkaline nature amounting to from 10 to 11% of the asbestos, were extracted. Successive extraction of the asbestos fibres at boiling temperature with caustic alkalies and nitric acid, followed by a thorough washing will free the asbestos of its alkalinity and other water soluble substances, the presence of which is to be regarded as extremely objectionable when the asbestos is used in the manufacture of filtermass.

C. Sellenschiedt[3] also warns against the use of inferior, imperfectly purified, asbestos pulp for filtration of beer. He found that this pulp when used is likely to give rise to a characteristic " blueish clay " turbidity in the beer which is very difficult to remove.

The determination of asbestos in filter mass is best undertaken in the following manner: A small sample of the mass is burned on the loop of a platinum wire. A mass which contains

[1]Wochenschr. Brau., 21, 547-8.

[2]Z. ges., Brauw., 35, 208.

[3]Wochenschr. Brau , 1904, 21, 144-5.

no asbestos leaves a very small amount of white or grey ash which easily crumbles. A mass containing asbestos leaves a hard residue, which viewed under the microscope has the appearance of a mass with fused ends, or that of a bundle of fibres, finely threaded, and highly refractive.

Infusorial Earth or *Kieselguhr*. This filtering medium consists almost exclusively of silica and resists the action of the strongest acids. Microscopical examination reveals it to be made up of minute silicious shields of diatoms. This structure renders it particularly suitable for the purpose of filtration, the enormous number of exceedingly small pores retaining even the minutest matter held in suspension in any liquid.

Of 40 samples of filtermass on the market which were analysed by the Wahl-Henius Institute, as to the nature of fibre, presence or absence of asbestos, and for ash, it was found that:

1. All except five samples were composed largely of cotton fibres. The five were composed of wood cellulose, three of them exhibiting the lignin reaction, one to a marked degree, this was found to be composed entirely of mechanical wood pulp. In a few of the samples occasional linen fibres were present. In one sample occasional ramie fibres could be identified. Hemp and jute were not represented in any of these samples.

2. In 33% of the samples asbestos was found present, in amounts varying from 2 to 5%. The fibres were usually long and uniform.

3. The percentage of ash from the samples containing no asbestos varied from 0.22-0.88% with an average of 0.44%. When asbestos was present the ash amounted to from 1.72-4.82%, with an average of 3.15%.

It is significant that only a few of the masses contained linen fibres, and only in very small quantities.

VALUATION OF FILTERMASS

In the valuation of filtermass the percentage of ether-soluble substances present should be given careful consideration.

In 1897, E. Prior[1] drew attention to the fact that a large number of cellulose preparations sold for filling beer filters are contaminated with a soapy or oily smell, and which when steeped in normal beer, distilled water or 4% alcohol, impart a repugnant and disagreeable flavor, of a decidedly oily nature, to the liquid. He found that the amounts of rancid oil that could be extracted from certain of the filtermasses examined amounted to from 0.25-0.36%. The presence of these oils was held responsible for the bad taste imparted to the beer. I examined a few samples of American mass in this direction recently, and found that while most of them contained less than 0.20% of oily substances, one sample contained 0.27%.

In a previous paper,[2] Prior had shown that the usual filter losses are doubled and trebled when substances are present which impart an obnoxious flavor to the beer, and recommends that the brewer test his purchases of this material, by picking a small sample in pieces and soaking it in beer for a few hours, and examining the flavor of the latter, when, if contaminated, the material should be rejected as unsuitable, since absolute (chemical) purity and freedom from flavor are indispensable conditions to its suitability.

I have found that by steeping in water containing about 5% of alcohol, as has also been recommended by other investigators, any off taste is more easily noticeable than when beer is used, where it is likely to be somewhat obscured by the bitter principles.

Prior has also examined chemically pure cotton filtermasses and considers these better adapted for this purpose than cellulose (chemical wood pulp), a view opposed to that of Will, less pressure being required to force the beer through the mass, and there being less likelihood of the flavor becoming contaminated, the cotton fibres consisting of almost pure cellulose, entirely free from taste or smell.

Detailed information as to the methods to be employed in the analysis of filtermass has been recently given by Zykes,[3]

[1]Bayerisches Brauer J., **7**, 133-4.
[2]Z. ges. Brauw , 19, 244.
[3]Z. ges. Brauw., **35**, 205-10.

and is here referred to, being the most complete treatise on the analysis of filtermass at present available. With the exception of the micro-chemical method of Hoehnel[1] the manner of conducting the various tests needs no further amplification.

In speaking of Hoehnel's micro-chemical method, Zykes emphasizes the fact that this is the only satisfactory method by means of which it has become possible to differentiate the different fibres micro-chemically, but fails to supply certain exact data which, unfortunately, are lacking in Hoehnel's own description of his method. In carrying out the test, which depends upon a color reaction of the cellulose with sulphuric acid and iodine, the concentration of the sulphuric acid employed is of utmost importance and unless the proper concentration be employed the test is unreliable. In order to determine this concentration Hoehnel suggests experimenting with known fibres, until it is found. This requires considerable time and experience and consequently limits the practical application of the test.

Having had but little experience in applied technical microscopy, I requested my friend and former co-worker P. Weber to investigate the Hoehnel method with reference to the examination of filtermass, in order to determine, if possible, the exact concentration of the standard sulphuric acid. After making a series of experiments using the reagents in proportions given by various investigators, he found that the reagents prepared according to Dannerth[2] gave the best results.

The method of work finally decided upon by him is the following.

REAGENTS

1.   Iodine Solution:
     Potassium Iodide 1 gram.
     Water (distilled) 100 cc.
     Iodine to excess.

After the solution is saturated at room temperature the excess of iodine is filtered off.

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[1] " Mikroskopie der Technisch Verwendeten Faserstoffe," 2nd Ed
[2] Dannerth, " The Methods of Textile Chemistry "

2. Sulphuric Acid:
      Sulphuric acid, (Sp. gr. 1.84) 30 cc.
      Water (distilled)   10 cc.
      Glycerine   20 cc.

Procedure: A small piece of filtermass, previously torn into bits is boiled for two minutes in a 4% solution of potassium hydrate, and then thoroughly washed with distilled water on a 100 mesh sieve. A small sample is then placed on a slide and the fibres separated as much as possible from one another by means of the teasing needles. The excess water is then removed by gently blotting them twice. A drop of iodine reagent is next applied to them and permitted to remain in contact with the fibres for 1½ minutes. The fibres are then again blotted. They are moistened with a drop of the sulphuric acid reagent, and after placing a glass cover upon them are ready for examination. The colors imparted to the various fibres, provided they are present, are the following:

Reddish-Violet Cotton.
              Linen.
              Hemp.
              White, bleached jute.

Blue   Chemical wood pulp.

Yellow   Mechanical wood pulp.
              Raw jute.

A filtermass of good quality should accordingly contain no fibres which turn yellow with Hoehnel's reagent, inasmuch as both mechanically prepared wood pulp and Raw Jute are inferior fibres, and should not occur in filtermass.

As regards the number of different tests which should be made with every mass received for examination, I would suggest the following eight, for the reasons mentioned, viz:

A. PHYSICAL EXAMINATION

    1. *Distribution in water.* Gives information as to whether the mass is likely to ball. By adding a few drops of an alcoholic solution of phenolphthalein to the mass so suspended in distilled water the neutrality of the mass can be tested. This shows whether the mass has been properly washed.

    2. *Taste imparted to 4% Alcohol.* The importance of this is obvious.

B. MICROSCOPICAL EXAMINATION

    By means of this examination the nature and length of the fibres, and degree of fineness can be determined. " The value of a filtermass depends largely on the degree of fineness possessed by the component fibres, the more delicate and finer these elements (wood-fibres and bastfibres) are, the higher will be the efficiency of the mass in regard to filtration."[1]

C. MICRO-CHEMICAL EXAMINATION

    This serves the purpose of verifying the results of the microscopical analysis and gives certainty as to the kind of fibres present, in the case of doubt.

D. CHEMICAL EXAMINATION

    1. *Percentage of Moisture.* Inasmuch as filtermass is usually sold by weight, moisture should be determined for the purpose of obtaining figures as to its commercial value, otherwise the determination is of little significance. The percentage of moisture may vary from 3-12%.

    2. *Ash.* This determination serves the purpose of furnishing data on the amounts of mineral constituents present in the mass. If the mass contains no asbestos, the ash should not amount to more than 1%. (Zykes, loco. cit.). In the presence of asbestos a corresponding increase is permissible.

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[1] Z. ges. Brauw., 35, 205-10.

3. *Ether-soluble substances.* The filter mass should not contain any fatty or resinous substances for reasons already given, furthermore, these are likely to exercise a detrimental influence upon the foam holding capacity of the beer. It has also been noted that masses containing resinous constituents do not distribute themselves uniformly in water.

4. *Lignin.* This test indicates the presence or absence of mechanical wood pulp and gives an insight into the commercial value of the mass. Woody fibre occasionally occurs in many of the vegetable fibres, but its presence is regarded as objectionable and lowers the economic value of the fibre. The reagent for this test is best made fresh, as it is likely to discolor if kept too long, especially on exposure to light. It is quickly prepared by dissolving some crystals of phloroglucin in say 5-10 cc of absolute alcohol and adding one half its volume of concentrated hydrochloric acid.

The above tests do not require much time and should be made with every sample received for examination. The results could be tabulated, the data being inserted, preferably in printed or mimiographed forms for that purpose, arranged somewhat in the following manner:

FILTERMASS

Date Sample was Rec'd......Quantity....How packed . ....
           Laboratory No .... Date of Report......

A. PHYSICAL EXAMINATION

Appearance, etc.	Distribution in water	Taste in 4% Alc.

B. MICROSCOPICAL EXAMINATION
   1. Nature of fibres......................
   2. Character of fibres....................

C. MICRO-CHEMICAL EXAMINATION
1. Color reaction according to Hoehnel............
2. Approximate Composition. ....%
...............%

D. CHEMICAL EXAMINATION
1. Reaction............ ....
2. Moisture.....................
3. Ash ....
4. Ether-soluble substances........
5. Lignin......................
REMARKS: ....

In addition to these determinations, Zykes suggests the following:

Water soluble substances: These should not exceed 0.2%.
Sulphurous Acid: a. Qualitatively.
                       b. Quantitatively.

Efficiency of filtration: This may be determined in a number of ways, but most of the known methods present more or less difficulties. According to one of the methods, the time required for a certain quantity of beer with yeast turbidity to filter clear through a Buechner filter packed with a given weight of mass, through which the beer is passed at a certain uniform pressure, is taken. A more practical apparatus for this purpose has been devised by Zykes[1] and is described by him. He found that the results obtained using this apparatus in almost every case showed good agreement with those in practice. Nevertheless, the results are of significance only from a comparative standpoint, and for this reason the usefulness of the determination is largely limited to the manufacturer's need, who may wish to compare a number of masses as to efficiency, either as regards speed, or effectiveness of filtration, *inter se.* In the brewers' laboratory the determination is of little value, inasmuch as usually only one mass is received at a time for examination, and it would, therefore, be necessary to have a standard with which the same could be compared. Furthermore, identical results, even in the hands of an

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[1]Allg. Z. Bierbr. u. Malzfabr. 39, 1911, Nr. 19.

experienced man are difficult to obtain where the same mass is used, which proves that it is practically impossible to have the conditions of the experiments always uniform.

Dreverhoff,[1] lays considerable import to the determination of the presence or absence of starch in filtermass, and suggests that the brewing industry employ only such masses as are free from starch. Brand,[2] discussing the view of Dreverhoff, states that he has been unable to find appreciable amounts of starch in any of the masses examined by him; Zykes,[3] has had similar experiences.

If cellulose is treated with acid, as it is customary in the process of purification, it will give a blue or bluish-purple coloration when brought in contact with iodine solution, and according to Brand this reaction may have been the one upon which Dreverhoff based the above mentioned conclusions. Starch, however, cannot be extracted by means of water from the masses exhibiting this reaction, nor can it be converted into sugar, and, therefore, cannot really be present.

There appears to be a view prevalent that the determination of resins is unnecessary. This is based on the argument that the brewer boils his filtermass prior to first use, as I understand, lately with the addition of small amounts of alkali, this treatment saponifying all resins of fatty substances likely to be present. The question, however, is this: Should this preliminary treatment be necessary with a filtermass of good quality? Should the mass that requires this treatment command the same price as the one that does not? I am of the opinion that it should not. The quantities of filtermass used annually by the larger breweries are such as to warrant an investigation into this question. I, therefore, urge that it be considered whether it is not advisable to take the presence of resins and lignin (present in mechanical wood pulp) into consideration in judging the value, especially the commercial value of filtermass.

Undue importance is being attached to a mass of pure white color, since mass having a somewhat brownish tint may be con-

[1]Z. fuer d. sacchs-thueringer Braugewerbe, **2**, No. 5.
[2]Zeit. f. d. ges. Brauwesen **24**, 322.
[3]Loco. cit.

stituted of fibres better in themselves than those of white appearance.   Filtermasses prepared from fustian, a coarse linen or cotton fabric, such as corduroy, are very satisfactory but seldom pure white in appearance, while on the other hand, it is easy to bleach cheap rags and mechanical wood pulp to give it a white appearance.   It must, however, be remembered that the presence of lignin in fibres causes these on exposure to air to discolor, wherefore the phloroglucin test becomes absolutely necessary when it is desired to determine whether the brownish tint is due to the presence of mechanical pulp or fibres of a desirable type characterized by this color.   Of course, microscopical examination would likewise serve to differentiate between the two possibilities, but a microscope might not be available where the chemical test would be.

As regards mechanical wood pulp, taking for granted that it is equal to chemical pulp as far as the filtration of beer is concerned, which still remains to be determined by practical experiments in the brewery, the question is should or should not the mechanical wood pulp be considered an adulterant when present in filtermass?   I am of the opinion that it should, and base my view on the following facts: In the first place, it is a well known fact that mechanical pulp is in every way inferior to chemical pulp as the following analysis partly shows:[1]

	Mechanical Spruce pulp	Chemical pulp from same wood
Cellulose	53.0	88.0
Resin	1 5	0.5
Aqueous Extract	2.5	0 5
Water	12.0	8.0
Lignin	30.5	2.5
Ash	0.5	0 5

Furthermore, the mechanical fibre is weaker, not uniform, and not durable.   In the second pace, the manufacturing cost of the mechanical pulp is considerably lower than that of chemical pulp and if a mass containing mechanical pulp, no matter how excellent in itself it may be, is sold at the same price as is a

[1]Syndall, " The Manufacture of Paper."

mass containing chemical pulp only, unless this is stated at the time of the purchase, the buyer is not being fairly dealt with. The mass containing chemical pulp should at all times command a higher market price.

With these suggestions, and let them be suggestions only, which I hope to bring before the practical man, whose experience enables him to judge them fairly, I wish to close the subject of my paper.

There is no doubt but that many of those superintending the working of the brewery have through long years of experience accumulated knowledge on the subject which, if published, would not only be incentive to further experiments, but would prove of great value to others in this industry.

Therefore, it appears not only most desirable, but urgent that more be published on this subject. It is not at all unlikely that, in the light of the recent remarkable advances in the manufactures, this may result in the discovery of some fibres or other materials which, although at present of no commercial value, could be converted into a filtering material which for the purpose of beer filtration may be equal, if not superior to, the masses now in use. It must be remembered that the brewing industry does not require such vast amounts of raw material as the paper making and textile trades, and therefore, that fibres which owing to a limited supply could never find introduction into these trades could be excellently utilized for the manufacture of filter mass. Such a discovery would unquestionably mean great economy to the brewing industry and without doubt also a generous bonus to the discoverer.

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THE VITICULTURAL INDUSTRY OF CALIFORNIA AND THE MANUFACTURE OF ITS WINES

By P. C. Rossi

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California produces all the raisins grown in the United States; three quarters of the Wine, and a large share of the shipping grapes. It is also beginning to attract attention with its Grape Juices, Grape Syrup and Wine Vinegar and is utilizing the by-products of the Vineyard in the manufacture of Cream of Tartar, Tartaric Acid and Rochelle Salts.

According to the closest estimates obtainable, there are to-day upwards of 275,000 acres in California devoted to grape cultivation. Of this acreage about one half, or 150,000 acres, is planted to grapes intended for the exclusive making of Wines. About 125,000 acres are devoted to the growing of table grapes and of grapes for raisin purpose. A large portion of these grapes, especially the second crop, is sent to the Distilleries to be made into brandy. A portion also of the first crop Muscat Grapes is made into a Wine called " Sweet Muscat " and also into fortified material for the making of Sherry.

During the past ten years, it is estimated that the manufacture of California Wines has almost doubled. In 1900 the output was about 25,000,000 gallons, of which about 15,000,000 was Dry Wines and 10,000,000 Sweet Wines. The yield of 1909 and 1910 averaged about 45,000,000 gallons for each year. The production of Sweet Wines will easily reach last year's record of 17,983,465 gallons while the Dry Wine output will total about 27,000,000 gals.

About 60,000 Vineyardists and Assistants are dependent upon the Viticultural Industry.

Wine-making is conducted on a very large scale, especially in the Sweet Wine Districts, where the Wineries are equipped for very rapid working up of grapes, some of them having a capacity

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of as high as seven hundred and fifty tons per day. These Grapes are brought to the Wineries, either by team, in which case, the grapes are thrown loose into the wagon and afterwards unloaded from the wagon by pitchfork into the hopper leading to the Crusher, or else, they come in bulk in cars, which have been lined with paraffined canvas in order to catch any juice which may be crushed out of them, either by their own weight, or, by the jarring of the cars in transit. It necessarily follows in conducting operations on such a scale that many of the grapes are not perfect; that is, some few on a bunch may have become moulded or spoilt. The grapes, themselves, carry on their skins, the necessary " Yeast Cells " (Saccharomyces) which are necessary to cause fermentation of the grape juice and produce alcohol. They also carry many bacteria of different species which can, if not properly controlled interfere very seriously with the proper fermentation of the true Wine Yeast and may, under some circumstances, if allowed to attain sufficient development, cause a very defective and inferior wine. Their action, if not checked, tends to produce faulty Fermentation and such ethers and acids of the higher series, as are foreign to the tartaric acid and ethers, produced by the natural fermentation of the grapes and consequently, any method which can control or abolish such action, will not only produce a more delicately flavored, but also, a purer and more wholesome wine.

It has been demonstrated that abnormal Yeasts and bacteria develop more rapidly in the early stages of fermentation than the true Wine Yeasts, especially in hot climates and during hot days, when the grapes are crushed warm and that they convert into undesirable substances, much of the grape sugar and other component parts of the grape juice which would, otherwise, be utilized by the true Wine Yeasts in producing the alcohol, ethers and other substances so necessary in the making of a high character of wine.

It is a well-known fact, as has been evidenced by the practice of centuries, that the use of sulphur fumes in empty casks or packages, which have previously contained wine, destroys the germs of all false ferments that may be present and, as a consequence prevents the starting up of injurious secondary fermen-

tation in wine, which may afterwards be placed in these packages or casks. During the last ten years, it has been the practice of the more advanced wine-makers in foreign wine-making countries, particularly in Algeria, France, Spain and Italy, to use small doses of sulphur dioxid, or, small doses of potassium metabisulphite immediately after the grapes are crushed, in order to control the growth of these Wild Yeasts during the fermenting period. It has been demonstrated by wine-makers abroad that the use of sulphur modifies and subdues the action of Wild Yeasts, while producing practically no effect upon the action of the true Wine Yeasts, which are thus allowed to proceed with the conversion of the grape juice into pure potable wine.

The Sweet Wine Makers of California, in fact, of the whole United States, are working under the Internal Revenue Law, known as the " Act of October 1st, 1890 " as amended at subsequent periods, one section of which provided that pure Sweet Wine, which may be fortified free of tax is fermented grape juice only and shall contain no other substance whatever, introduced before, at the time of, or after fermentation, except as therein expressly provided.

Under this provision, the Commission of Internal Revenue has ruled against the use of sulphur in any quantity in the wine before the fortification of the same by the addition of Grape Spirits, although he has the power to allow this, if showing can be made that the process is not contrary to the intent of the Law, for it is simply pertaining to the Cellar treatment for the proper making of the wine. The advantages of such use of small doses of sulphur have been taken up with the Honorable Commissioner of Internal Revenue and he has expressed an opinion that " Should a Ruling be secured from the Department of Agriculture, that the use of sulphur in the manner outlined, would not prevent the labelling of the product as Pure Sweet Wine, that, in such case, he would be disposed to give the matter further consideration."

In contending for the advantages secured by using small doses of sulphur Dioxid in the manufacture of Sweet Wines, I submit that while Sweet Wines have been made and can continue to be made, as before, without the use of sulphur during fermentation they are frequently inferior and it is better for the Industry: for

the Consumer, and for the Authorities, who are controlling the manufacture of wine to adopt methods that have been developed by the latest scientific discoveries, and encourage rather than prohibit the use of small quantities of sulphur, through which a sound clean product is obtained, without any unpleasant odors, flavors, or defective volatile acids. I believe the authorities should grant the necessary permission for the use of sulphur dioxid and follow in the wake of progressive wine-makers in other countries. The dose of sulphur dioxid recommended by the Professors of Viticulture vary from 75 to 250 milligrams per litre of Must, according to the condition and the temperature of the grapes at the crushing time, as well as the temperature during the fermenting period. It has been demonstrated by all the chemical analyses made of the Must treated with sulphur dioxid before and after fermentation, that the quantity of SO_2 in the Must does not vary during the first few hours, or, the first day or two, or, as long as the Must does not begin to ferment, but, as soon as the fermentation begins 50% of the SO_2 added, disappears gradually during the first day and the balance disappears in the next few days, leaving only traces in the fermented wine.

As the Regulations stand at present, an inferior grade of wine (deteriorated by acids and ethers produced through faulty fermentation) can be labelled " Pure," when, as a matter of fact, it is far from pure and no protection whatever is afforded to the consumer. On the other hand the faulty fermentation can be prevented by the use of small doses of sulphur dioxid during fermentation and it seems to me that any process which will tend to the making of purer wine (thus following out the *intent* of the Sweet Wine Law) should be encouraged, both by the Pure Food and Internal Revenue Authorities and conversely, that it is illogical and contrary to the intent of the Pure Sweet Wine Law, to prevent, through lack of necessary permission, the making of a purer wine than is now possible under existing Regulations.

Having asked the opinion of Mr. Frederick T. Bioletti, Professor of Viticulture in the University of California, as to whether Sulphur Dioxid or its preparation were useful and its use advisable in the manufacture of Sweet Wines, and also, whether its use

would constitute the addition of a foreign substance to the grapes, I was pleased to receive his answer as follows:

" With regard to the first point, I can simply reiterate what I have already written to you regarding the use of sulphurous acid in the manufacture of Dry Wine.

" The proper fermentations of Sweet Wines and of Dry Wines are identical in character as far as regards the yeasts. What is necessary to cause a clean, pure, wholesome fermentation in one case, is necessary in the other.

" The judicious use of sulphurous acid, whether in the form of sulphur fumes, potassium meta bisulphite or the liquified gas during and before fermentation, has resulted in great improvements in the quality of all wines and has greatly diminished the amount of spoilt and unwholesome wine which was formerly made. On this point, *all* expert wine-makers and *all* competent enological investigators agree.

" While there is less danger of the complete spoiling of Sweet Wines by injurious fermentation than there is of that of Dry Wines, imperfect fermentations often much deteriorate their quality. Volatile acids, persistent cloudiness, unpleasant flavors and odors, are caused principally by the development of bacteria, moulds and wild yeasts. Much of this damage may occur during the first stages of fermentation in Sweet as in Dry Wine. There is no method known to practice or science of effectively preventing these defects without introducing others except the accurate and careful use of sulphurous acid.

" Much of the opposition to the use of sulphurous acid on the part of those unfamiliar with the theory and practice of wine-making comes apparently from a misconception as to its object. Sulphurous acid is not used by the Wine-maker as a *preservative*. The amount necessary for this purpose would be sufficient to completely spoil his wine and to render it unmarketable. Used properly, it is no more a preservative than the steam he uses to clean and sterilize his barrels. Wines properly fermented by the use of minute but accurately measured amounts of sulphurous acid have superior keeping qualities but not because of the presence of sulphurous acid. This, in the finished wine, has in great part disappeared and what remains has entered into inoccu-

ous combinations and lost its antiseptic properties. Such wines keep better because the yeast has done its work better, and has utilized the sugar, albuminoids and other matters acted upon by micro-organisms to produce substances of value, and not deleterious to the wine, as are those produced by the other organisms which would have developed had no sulphurous acid been used.

" My opinion on the first point, therefore, is that sulphurous acid is useful in the fermentation of Sweet Wine and necessary in most cases for the production of Sweet Wines of the highest quality.

" The second point involves an interpretation of the Sweet Wine Law. This Law expressly excludes the addition of any substance whatever to the grapes except sugar ' for the sole purpose of perfecting Sweet Wine according to commercial standard,' or, ' water in such quantities only as may be necessary to the mechanical operations of grape conveyers.' These exceptions seem to show that the purpose of the exclusion of foreign substances is to prevent the use of substitutes for grape juice. The addition of sugar to improve the grapes, or, of water to facilitate their handling are specifically allowed.

" The question, therefore, resolves itself into this: Does the use of sulphurous acid constitute an addition of a foreign substance in the sense intended by the Sweet Wine Law? *I believe it does not.* This opinion is based on my knowledge of wine-making and of the interpretations of Pure Food Laws in various Countries.

" ' Wine,' is defined by the United States ' Standard of Purity for Food Products ' as ' the product made by the normal fermentation of the juice of sound, ripe grapes and the usual cellar treatment.' Similar definitions are adopted in European Pure Food Laws. The words ' usual Cellar treatment ' have been always held to include the use of findings and that of sulphurous acid, as they constitute essential parts of the manufacturing process.

" It would be as logical to forbid aeration of the grape juice as to forbid sulphuring. Aeration introduces oxygen; sulphuring, sulphurous acid. Either of these practices carried to excess will spoil the Wine. Either of them omitted entirely will result in

inferior wine. This is true for both Dry and Sweet Wines. The best wine in both cases can be made only by the proper use of both the oxygen of the air and sulphurous acid.

" The use of the necessary minute quantities of sulphurous acid, therefore, seems to me to be no more an addition of a foreign substance, than the use of eggs, gelatine, tannin and aeration, all of which are properly permitted in the manufacture of all kinds of Wines."

I have thought it advisable to call the attention of the VIII International Congress to this subject, it being of such immense importance to the Viticultural Industry of California, and I trust it may be deemed worthy of discussion by our foreign expert guests.

ON BACILLUS NATTO

By S. Sawamura

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Natto is an article of food prepared by leaving boiled soya-beans wrapped in rice straw in a warm place for a night, and thus making them ferment. Soya-beans of natto are coated with a characteristic slimy substance. The author[1] separated formerly two species of bacilli from natto obtained in Tokyo, No. 1 of which produced good flavored natto when inoculated to boiled soya-beans, and No. 2 strongly slimy one. The former bacillus was considered to be the chief actor in natto fermentation and received the name of " Bacillus natto." In later years the author examined bacteriologically many samples of natto obtained at various localities, and found that the producer of natto is the same in all cases, viz. " Bacillus natto." This bacillus can produce natto of good flavor and strong viscosity, and the presence of other microbes is not necessary in the fermentation of natto. The bacteriological description of Bacillus natto is as follows:

FORM: The bacillus measures 1 m in width and 2—3m in length. The ends of the rod are round, and the bacilli unite in twos or more.

MOBILITY: Motile.

SPORE-FORMATION: The bacillus forms a spore mostly in the middle of the cell.

GRAM'S METHOD: It is not decolorized by Gram's method.

OXYGEN: Aerobic.

BOUILLON: It produces a light brown, thin, characteristic dry, mealy scum which is broken into pieces by shaking. Bouillon does not become turbid.

PEPTON WATER: The scum formation is the same as in bouillon, but its color is lighter.

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[1]Bulletin of Agricultural College, Tokio, vol. VII, p. 107.

AGAR PLATE CULTURE: The colony is light brown and flat, and has a characteristic dry, mealy appearance, and a small point in the centre of the colony, the periphery of which is irregular and divided featherlike. It produces a smell like natto.

GELATINE PLATE CULTURE: Small colonies are formed which liquefy gelatine quickly.

AGAR STREAK CULTURE: It produces light brown, flat and characteristic dry mealy colony.

GELATINE STREAK CULTURE: It is quickly liquefied along the needle track.

AGAR STAB CULTURE: It grows only along the needle track and forms no branch.

GELATINE STAB CULTURE: It is liquefied along the needle track.

SOYA BEAN AGAR: The colony has folds and is rougher than on bouillon agar.

POTATO: Gray slimy colony with many folds, resembling that of potato-bacillus.

GAS: It is not evolved in glucose bouillon.

AZOLITHMIN-MILK: It is reddened at first, and then decolorized, and the milk becomes clear. After many days azolithmin is turned somewhat blue when it is newly added.

INDOL: Pepton water culture kept at 32° C. for 7 days gives the characteristic reaction, neither with $NaNo_2$ and H_2SO_4, nor with nitroprussic acid and NaoH.

H_2S: It is not formed.

It was confirmed by the previous investigation that Bacillus natto produces trypsin-like emzym, and decomposes protein of soya-beans. In order to know how a protein is decomposed by this bacillus, boiled soya-beans were inoculated with this bacillus and kept at 35° C., one sample for 14 hours and the other for 7 days. The viscosity and flavor of natto thus prepared are stronger in the younger than in the elder.

The nitrogen in various forms and soluble organic matter in per cent. of the dry matter were found to be as follows:—

	14 hours	7 days
Total nitrogen	7.363	7.421
Insoluble albuminous nitrogen	5.881	2.104

Soluble albuminous nitrogen	1.482	5.317
Soluble coagulable albuminous nitrogen	0.307	0.182
Soluble uncoagulable albuminous nitrogen	0.321	0.477
Nitrogen of pepton and polypeptides	0.208	0.408
" " arginin, histidin and lysin	0.069	0.085
" " purin bases	0.086	0.140
" precipitated by phosphotungstic method	0.109	2.111
Soluble organic matter	21.947	41.546

Soya-bean contains nitrogen chiefly in the form of protein (85-90%), non-albuminous nitrogen being very little (10-15%).

Bacillus natto produces diastase, but reducing sugar was not found in natto thus prepared. This is probably due to the fact that soya-bean does not contain much starch, the main part of carbohydrate being in the form of galactan, etc., wherefore the little glucose formed was decomposed again by the bacillus.

The author expresses hereby sincere thanks to Mr. Oshima, assistant of the College, who analysed natto as above mentioned.

INORGANIC COLLOIDS FOR CLARIFYING LIQUIDS

By F. P. Siebel, Ph. C.

The Zymotechnic Institute, Chicago, Ill.

Progress in that department of Science now indicated by the term " Colloidal Chemistry " had been comparatively slow until the introduction of the Ultramicroscope or rather until scientists had with the aid of this instrument been enabled to study the true nature of the solutions and suspensions, and thereby obtained a more correct conception of that peculiar condition, designated as " Colloidal " in which many substances had been known to exist.

Of comparatively recent dates are those investigations made with reference to certain phenomena depending upon the presence in beer of a rather complex mixture of colloids of varying composition, the equilibrium of which is most easily disturbed by reason of the many and extreme changes to which beer is subjected and producing in this way very undesirable results.

However while these organic colloids are of great significance with regard to some of the more characteristic properties of beer, such as foam holding capacity and brilliancy, there are nevertheless also a number of inorganic colloids, which are of equal if indeed not of greater importance, at least in some respects, some of which may be destined to take the place of certain organic colloids employed in the production of beer which have hitherto not received much attention.

It is for this reason that I consider this an opportune time and place to bring to your attention the studies and investigations made in this regard, selecting as a subject for my paper, the use of inorganic colloids for the clarification of liquids.

The use of alum for the treatment of water with special reference to its clarification has been known for many years, while the introduction of a closely related compound, aluminum

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The use of alum for the treatment of water with special reference to its clarification has been known for many years, while the introduction of a closely related compound, aluminum

hydrate, for similar purposes is of comparatively more recent date.

The effect of these two substances, which are both inorganic in nature, is based upon the fact that aluminum hydrate is truly colloidal, and deposits from a solution as a hydrogel, which also takes place with alum, which is decomposed by the carbonates mostly contained in all natural waters.

While the clarifying agents just referred to are well adapted for water or similar neutral and indifferent liquids, their use is excluded for acid liquids or liquids which are susceptible to an effect on their taste, or other characteristic properties, and therefore other means had to be sought.

By investigations instituted at the Zymotechnic Institute many years ago, it was demonstrated that another colloid of inorganic nature, which in such instances can serve the intended purposes is silicic acid, which can easily be obtained in a colloidal solution, from which it separates in a gelatinous form.

Since silicic acid unlike alum possesses no taste and unlike aluminum hydrate, is not affected by weak acids, such as lactic acid contained in beer, it is therefore particularly well adaptable in this instance.

The mode of using silicic acid as a clarifying medium, is either by using directly dialyzed solutions or by producing its colloidal within the liquid which is to be clarified by decomposing in a suitable manner convenient solutions of soluble silicates.

In the case of beer or wine, such a decomposition can be brought about by the free acid contained in these beverages such as lactic, tartaric, malic, and succinic acid, thereby making it unnecessary to introduce other substances into liquids of this nature that are to be clarified, than the solution of the silicates whereby a material alteration in the composition of the respective product is prevented.

However it would be preferable to use the dialyzed colloidal solution of silicic acid, thus obviating the introduction of any foreign material which might be retained by the beer or wine and avoiding thereby any objections which might be made on account of pure food legislation.

SOURCES OF ERROR IN THE DETERMINATION OF THE ACIDITY IN WORT AND BEER

By F. Stuhlmann

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Among the constituents of the extract contained in wort or beer, we find a number of substances which, though not very considerable in quantity, are nevertheless of the highest importance with regard to the quality of the beer, particularly as far as taste, character and stability of the same are concerned.

This group comprises those components of the extract which are characterized by their acid properties and of which lactic acid, succinic acid, acetic acid, and especially acid phosphates aside of others, may be mentioned as the most important.

In reporting the analytical results of an analysis of either wort or beer, it is customary to state this acidity as " total acidity, calculated as lactic acid," and the determination of the same is generally made by titration with a convenient solution of alkali, using as indicator " neutral " litmus.

However, since this indicator is equally sensitive to free acid as well as to the acid-reacting phosphates, it is apparent that by this method it is not possible to differentiate between the two and therefore such a determination does not furnish any information whatever as to the relative amount of free acids, particularly lactic acid and the amount of acid phosphates contained in wort or beer.

This however is the very point of importance inasmuch as acidity caused by lactic acid will, in many instances, have an entirely different significance from an identical degree of acidity, caused by an equivalent amount of acid phosphate, as can probably be best illustrated by the following example:

Suppose two different brewing materials would yield to a wort practically the same " total acidity," f. i. 0.042%, calculated as lactic acid, of which let it be assumed, in the case of the

first material 0.020% be really lactic acid, while in the second case the same may be 0.12%, the balance in both instances being due to phosphates.

Then it becomes apparent, that if identical brews were made from each one of these two materials, using as brewing liquor a water of sufficient alkalinity to neutralize 0.15% of lactic acid, the resulting worts would be of entirely different composition, although the " total acidity " would be practically the same.

The wort from the first one of these two materials would still contain some free lactic acid, while in the second, only acid phosphate would be present.

There is no question that these two conditions are of widely different effect upon the wort during the subsequent stages of fermentation, storage, clarification, etc., however as stated the " total acidity " being the same, a titration of the same, using neutral litmus as indicator will not indicate any such difference.

Aside from this, the customary way to state simply "total acidity," calculated as lactic acid, can easily lead to considerable misunderstanding.

It may, for example, occur that on the one side a sample of beer, having 0.16% of "total acidity" could still be considered normal, while it may become necessary that another sample of beer, containing 0.15% be proclaimed sour (this depending entirely upon whether the respective acidity is attributable more to acid phosphate or more to free acid), which in the absence of any further explanation must look inconsistent and without doubt will cause misunderstanding.

Hence it appears not only desirable, but rather important, that for the determination of the acidity in wort and beer a more adequate method be adopted which permits of a differentiation between acidity caused by free acid, on the one side and acidity caused by acid phosphate on the other.

A suggestion how such a method could probably be arrived at, may possibly be offered by the following series of tests, which plainly demonstrate that this difference in the nature of the acidity manifests itself also during a titration, provided a suitable indicator is selected.

For these investigations, solutions were prepared containing:

1. Lactic acid   0.108%   Monosodium phosphate   none
2. Lactic acid   0.027%   Monosodium phosphate 0.036%
3. Lactic acid   0.027%   Monosodium phosphate 0.108%
4. Lactic acid   none   Monosodium phosphate 0.144%

These four solutions were titrated with the necessary precautions, once using neutral litmus paper as indicator, and a second time using red litmus paper.

With neutral litmus—100cc each of these solutions required for neutralization 12.1cc, 11.9cc, 11.8cc and 12.0cc of n/10 alkali respectively, corresponding to 0.109%, 0.107%, 0.106% and 0.108% or practically the same total acidity, if calculated as lactic acid.

Titrating however when using red litmus as indicator, the point of neutralization as indicated by the appearance of the neutral tint of litmus on the test paper, was attained at 12.0cc, 9.9cc, 4.3cc and 2.1cc of deci-normal alkali respectively.

Comparing these results with those obtained in the first series, it becomes evident, that:

1. In the case of a liquid containing lactic acid only, both indicators show the presence of the acid practically to the same point.

2. In the case of a mixture of lactic acid and an acid phosphate, the former predominating, red litmus indicates total disappearance of acid at an earlier period.

3. In the case of a mixture of lactic acid and acid phosphate, the latter predominating, the point of neutralization is indicated by red litmus at a still earlier state, and

4. In the case of a solution containing monosodium-phosphate only, the acid reaction upon red litmus is extinguished at the earliest moment.

It will however also be noticed that in the case of solutions, containing both free lactic acid and acid phosphate, the titration with red litmus exceeds the amount of lactic acid. The reason for this becomes apparent from the titration of solution No. 4, which contains no free acid, whatever, but nevertheless requires 2.1cc. of n/10 alkali for 100cc. until neutralization against red litmus is

attained, which apparently is the case as soon as by the titration di-sodium-phosphate has been formed in a quantity sufficient to balance the acid reaction of the monosodium-phosphate.

While the limited space does not permit here to go further into this subject, particularly with reference to the ratio in which the reaction upon red litmus of these two phosphates will balance each other, from which the necessary method of calculating the results of such a titration can be deduced the foregoing will eventually be sufficient as a suggestion for devising a method of titrating the acidity of wort and beer, by which at least some information as to the nature of this acidity is obtainable.

ON THE BUDDING FUNGI OF "SHOJU-MOROMI"[1]

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Introduction

Up to now several studies on the budding fungi of "Shoju-Moromi" have been published, but with regard to the botanical classification all these studies have only little merit as we can not derive any systematical classification therefrom.

K. Saito,[2] in his first report on the microbes of "Shoju," enumerated Saccharomyces soja, soy-film-yeast, Pichia farinosa and one species each of Mycoderma and Torula. Afterwards he gave the soy-film-yeast the name of Zygosaccharomyces japanicus[3] though the conditions of the cell-fusion and the sporulation of this species have not been fully described. T. Nishimura,[4] who published his fruitful investigation on "Shoju," isolated three species of Torula under the names of Torula shoju, Torula shoju var. minuta and Torula turbinata. According to his investigation these three Torula species seem to play an important rôle in the brewing of "Shoju." Further he found several kinds of film forming species, two of which belong to the genus Pichia and others to Mycoderma and Torula. T. Mitsuda[5] studied five varieties of "Shoju-yeast," but all his yeasts have not the faculty of sporulation.

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[1] "Shoju-Moromi" (Soy mash) is prepared by mixing "Shoju-Koji," common salt and water in certain proportion. The preparation of "Shoju-Koji" is similar to that of rice or "Saké-Koji," but in the former steamed soy-bean and roasted wheat are used instead of rice.

[2] Cent. f. Bak. II Ab. XVII. 1906.

[3] The Botanical Magazine (Tokyo) XXIII 1909 p. 96. Cent. f. Bak. XXVI 1910. S. 93.

[4] Jour. of Scientific Agric. Society (Nōgaku Kwai Hō).

[5] Jour. of College of Agric. Tokyo Imp. Univ. Vol. I. No. 3. p. 347.

While G. Kita[1] found two species of Torula and a species which belongs to Saccharomyces, his description is too short to compare with the preceding studies. From these points of view, we come to the conclusion that "Shoju-yeasts" are not classified systematically. It need not be considered strange that such different analytical results have been stated by several authors, as the samples used for the isolation of yeasts differed from each other, not only as to the factories which supplied the samples, but also as to the kinds and qualities of the raw materials, and further in the manners of preparation ripening stages of "Shoju-Moromi." Nishimura, Mitsuda[2] and Kita in vain tried spore cultures of their yeasts after the gypsum-blocks-method, and they regarded their yeasts as Torula species. But we believe that there might be a great dissimilarity between the physiological conditions of the budding fungi of "Shoju-Moromi" which is distinguished from others by its rich content of common salt, and those of the budding fungi in every other fermenting mash. The necessary favorable conditions, under which even these particular yeasts can as easily produce spores as any other kind of saccharomycetaceae, might be prevented by some unknown factores. Although the specific differentiation of "Shoju-yeast" is not our only object, yet we believe that it is also important to give a satisfactory solution on this subject for both scientists and manufactures. Moreover there are many other points requiring further investigation, so these circumstances led us to make some researches on "Shoju-yeasts."

ISOLATION OF THE BUDDING FUNGI FROM "SHOJU-MOROMI."

Fifty-two samples[3] which were at different stages of the ripening process, were taken from eleven different factories[4] situated in various parts of our country, in order to gather as much as possible all existing kinds of the Budding fungi.

[1]Jour. of Chemic. Indust. (Tokyo) XIV, 156.
[2]Mitsuda did not classify his yeasts from a special point of view.
[3]Ages of "Moromi" were at different periods between 2-24 months.
[4]The following are the factories which very kindly granted us the samples:
Sh. Magi's "Shoju"-brewery at Noda in the province of Shimōsa.

To separate the budding fungi from each other in the samples we started from plate-culture using " Shoju-Koji "-agar as the culture medium. Further the cells, developed on the medium from different colonies, have been purified by Lindner's droplet culture.

The following budding fungi were isolated from the samples:

1. Zygosaccharomyces major, nov. spec.
2. Zygosaccharomyces Soja, nov. spec.
3. Zygosaccharomyces japonicus, Saito.[1]
4. Zygosaccharomyces Salsus, nov. spec.
5. An asporogenic species of Zygosaccharomyces(?).
6. A species of Mycoderma.
7. A species of Pichia.
8. Several species of Torula.
9. A species of Monilia.

INVESTIGATION ON THE FORMATION AND GERMINATION OF ASCO-
SPORES OF " SHOJU-YEAST."

Forms of cell and spore, production of film, and conditions of reproduction and sporulation, and further enzymatic actions are important factors for the classification of an yeast. Above all, determination of sporulation is perhaps one of the most important factors in the case of classification of " Shoju-yeast."

Saccharomyces soja, Saito[2] seems to be identical with Torula Shoju, Nishimura[3] (perhaps also with G. Kita's " Shoju "-yeast

S. Magi's " Shoju "-brewery at Noda in the province of Shimōsa.
Hamaguchi's " Shoju "-brewery at Chōshi in the province of Shimōsa.
G. Tanaka's " Shoju "-brewery at Chōshi in the province of Shimōsa.
J. Iwasaki's " Shoju "-brewery at Chōshi in the province of Shimōsa.
K. Nakamura's " Shoju "-brewery at Gaju in the province of Owari.
Asai-" Shoju "-brewery company at Tatsuno in the province of Harima.
Maruo-" Shoju "-brewery company at Tatsuno in the province of Harima.
Kikuichi " Shoju "-brewery company at Tatsuno in the province of Harima.
Takano's " Shoju "-brewery at Tatsuno in the province of Harima.
Kagawa " Shoju "-brewery experimental station at Shōtoshima in the province of Sanuki.

[1] The Botanical Magazine (Tokyo) XXIII, Cent. f. Bak. II Abt. XXVI 1910. S. 93.
[2] Cent. f. Bak. II Abt. XVII.
[3] Nogaku Kwai Hō.

No. 1)[1] in the micological relations except that the former fer-
ments galactose and can produce spores while the latter does not.

It is necessary to ascertain closely whether galactose is fer-
mentable or not by both yeasts since the determination of fer-
mentability of galactose is difficult compared with that of any
other sugar. To determine the possibility of sporulation of
"Shoju-yeast," of course, it is necessary not only to refer to all
the methods recommended for spore culture, but also to modify
them, further to establish other suitable methods. Also a species
whom we gave the name of Zygosaccharomyces soja seems to
stand in close relation with the preceding two yeasts. Therefore,
at first, we started to determine the relation in question from the
sporogenical point of view, and we repeated spore culture with
this yeast after the following methods: (a) gypsum block-method
improved by Hansen, (b) Kloecker's gypsum block-method which
immerses the gypsum block in wort instead of water,[2] (c) Schoen-
ing's gypsum block-method,[3] (d) methods of spreading yeasts
on the thin stratum of gelatine, prepared with, or without a
nutrient solution, likewise in yeast water and in sterilized water,
(e) Kohl's spore culture methods,[4] (f) Beijerink's agar medium
method,[5] (g) Gorodkowa's method.[6] Moreover we examined
the cells not only of old cultures on the slices of potato and carrot
but also of the yeast ring or film formed in " Koji "-extract, wort-
and glucose-yeast water-culture. In the preceding six different
cultures (a-f) which were kept for 2-20 days at 15°-35° C., a few
round, highly refractive, spore-like granules were often observed
in abnormal cells, however, these granules were never stained
red by double staining at all. On Gorodkowa's medium which
was kept at 28° C., we discovered some dumb-bell-shaped cells
after 6 days, and large numbers of small daughter cells which
connected together on mother cells after 15 days. Further we

[1] Jour. of Chemic. Industry (Tokyo) XIV 156.
[2] Zygosaccharomyces prioranus, Kloecker forms large numbers of sporu-
lated cells on this block; Handbuch d. Tech. Mikolog., Lafer, IV. 182.
[3] Ibid. 29.
[4] Die Hefepilye. Kohl 197.
[5] Cent. f. Bak. II Abt. IV. 657.
[6] Ibid. XXIV. 318.   ✱

observed rarely dumb-bell-shaped, ascus-like cells which contain 1-4 of spore-like globules after 3 months. Although we did not try to ascertain whether these globules are capable to germinate or not, they were easily stained by the double staining method.

Sporulation also has never occurred in the cultures of potato, carrot and glucose-yeast water. Now there is left nothing but ' Koji "-extract or wort-culture to give the last determination for sporulation of this yeast. It will not be useless to give the following details about the cells of yeast ring developed in " Koji "-extract or wort-culture which were kept for two months at room temperature.

(a) The forms of the cells, from which yeast ring is constructed, are so various that we could easily observe not only round or dumb-bell-shaped cells, but also highly elongated, mycerial cells or the cells which are similar to the permanent cells and the film cells of the first generation which Will[1] had closely investigated with some bottom yeasts.

(b) Sometimes we found a number of round, refractive granules in some dumb-bell-shaped cells.

(c) Most of the cells which formed yeast ring were stained with 0.5% methylen blue solution and Gram's solution, while the cells which contain a number of refractive spore-like granules were never stained with these solutions.

(e) The dimensions of these granules were so various that the largest one is in size of 5 u while the smallest one is 0.5 u.

(f) By double staining method these spore-like granules were never stained intensely red.

Hence we were obliged to observe whether these spore-like granules are capable of germinating. Each drop of " Koji "-extract, in which a few cells containing the spore-like granules were distributed well, was transferred on a cover glass, and then it was put on a hollowed object glass or Boettcher's moist chamber, being sealed with paraffin to prevent the evaporation of water. Such cultures were kept at various temperatures for several days but they have not changed at all.

[1]Handb. f. Tech. mykolog. Lafer. IV. 17-18.

K. Saito often observed some sporulated cells in yeast ring developed in " Koji "-extract, in which he cultured his " Shoju "-yeast, but he says nothing about any other conditions which have influence on the sporulation. Therefore, to determine more closely the individual conditions which influence the sporulation of our yeast we cultured the yeast in " Koji "-extract for 3 or 6 months at various temperatures extending from 17° to 25° C.

The cells which are similar to the sporulated cells of Saito's yeast have very rarely been observed in some yeast rings, and spore-like globules which occur in these cells were distinguished from the round, refractive granules as already mentioned. These cells showed also the forms of dumb-bell or like bodies. The globules which occurred in a mother cell were always transparent, round or oval, and contained a few tiny grains respectively.

In such respects these cells seem to coincide with the sporulated cells of Saito's yeast, but unfortunately, since these ascus-like cells were discovered too rarely to observe their germination, we were obliged to satisfy ourselves only by trying the double staining method for spore-determination. According to this double staining only the content of spore-like globules was stained red, and it was clearly distinguished from its wall.

Hence it becomes probable to conclude that specific differentiations of " Shoju "-yeasts have not coincided with one another owing to their sporulating difficulties.

Now after trying all these methods, we must discover some favorable conditions, under which even this obstinate yeast can easily produce its spore.

When we observed the cells of an yeast ring developed in diluted " Shoju " culture[1] of Zygosaccharomyces soja, we happened to recognize large numbers of dumb-bell-shaped cells which contain 1-4 of transparent spore-like globules. Moreover, it was clearly brought to light that these particular globules are real ascuspore by culturing these dumb-bell-shaped cells in Boettcher's moist

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[1] " Shoju " (commonly contains 15-17% Nacl) was diluted with water to make its salt content 5%, and was sterilised intermittingly in Koch's steriliser for 3 days. After the inoculation of Zygosaccharomyces soja it was kept in a thermostat at 22° C. for 15 days.

chamber which was laid under a microscope in warming apparatus (at 35° C). In these germinal culture we studied that these globules swell up to a considerable size, and put forth a bed and hence forward behave like vegetable cells. Moreover these globules were always stained red by double staining method, and yellowish blue with Gram's solution.

It is a remarkable fact that every spore of all the Zygosaccharomyces isolated from " Shoju-Moromi " stains yellowish blue with Gram's solution.

In order to decide whether sporulation of " Shoju "-yeast will be influenced by dilutions of " Shoju," contents of salt or kinds of nutrient fluid, and further by temperatures, we kept the cultures at various temperatures using " Koji "-extract or diluted " Shoju " which contained different quantities of salt. These experiments showed that sporulation of this yeast occurs earliest in yeast ring developed in sterilised diluted " Shoju " which was made to contain 4-5% salt by adding a sufficient quantity of water.

But it must be borne in mind that sporulation of this yeast is to be influenced by dilution of " Shoju " and temperature of the culture.

We observed large numbers of sporulated cells in the diluted " Shoju "-culture which was kept at 28° C. for the first 3 days and then at 20°-25° C. for 10 days. On the contrary, sporulation has not been observed in the same medium which was kept always at 28° C. for 20 days. In the case of " Koji "-extract which contains 2-7% Nacl, being treated after above conditions, sporulation has also been observed in yeast ring after the same number of days, but the number of sporulated cells was less than that in the case of diluted " Shoju."

Therefore, if it be desired to study the process of sporulation of " Shoju "-yeast it should be undertaken in the following ways:

(1)   The yeast is sowed in a sterilised test tube which contains a quantity of diluted " Shoju " (5% Nacl), and the culture is laid at 28° C. for first 3 days and then immediately kept at 20°-25° C. for several days.

(2)   When well defined yeast ring develops along the wall of the tube a few parts of the ring are examined under a microscope. As soon as a number of beak-shaped cells is observed, a small portion of the ring must be distributed in water in a sterilised Petri-dish.

(3)   A cover glass, on which the water is dropped, is put on Boettcher's moist chamber, and sealed with paraffin to prevent the evaporation of water.

(4)   It is observed under a microscope keeping it at 20° C.

According to the above treatments we can easily find that sporulation of our Zygosaccharomyces occurs in the following manner:

Two cells close to each other force up beak-like tubes and fuse together by growing up their length against each other, and accumulate their plasmatic granules towards the contact canals (glycogen reaction is especially remarkable in this contact canal). The wall in the contact canal breaks out of itself, and the plasma in one side or both sides of the ascus separates itself into a number of vacuole-like balls, which correspond to those of spores. Since these balls become surrounded with the plasmatic granules, the process of sporulation is not distinctly visible.   The spores are matured after 24 hours and contain a few tiny grains and are transparent, round or oval.

Although the total numbers of the spore in each ascus is 1-4 (mostly 4), the numbers of spores which occur in each part of an ascus are very variable.

It is not rare to find that spores occur in only one part of an ascus, in this case, sometimes a few portions of the plasma of other parts remain in the contact canal as if the rest plasma were lugged into one part which produced the spores.

A.   Non Film-forming Zygosaccharomyces

I.   *Zygosaccharomyces major, nov. spec.*

Since this yeast was mostly isolated from the samples of mature stage, it seems to play an important rôle on the ripening of "Shoju."

I. FORM AND SIZE. In " Koji "-extract or wort culture (4 days at 20° C.) cells are mainly spherical (3.7-7.5 u), sometimes oval, and their contents are homogeneous and exhibit sometimes vacuoles. The glycogen reaction is evident in every cell. Cells in yeast ring of " Koji "-extract culture (after 20 days at 20° C.) are so irregular that a small cell is in size of 2.5 u while larger ones up to 10 u. The occurrence of these cells seems to be somewhat prolonged in wort or " Koji "-extract which contain a quantity of salt. Old culture in the same media (2-6 months at room temperature) exhibits not only the cells which are similar to Will's film cells of the first generation, and permanent cells, but also very highly elongated, mycerial ones.

II. GROWTH. (a) Solid culture: Plate culture (7 days at room temperature): In " Koji "-extract or wort gelatine this species forms white greyish, round, bright waxy colonies. Streak culture: On " Koji "-extract-agar (30 days at 27° C.) it grows with somewhat brownish, waxy, dull lustered, elevated covering. Margin shows somewhat paralleled streamy canals. On glucose-sake-agar (10 days at 25° C.) it forms a greyish white, waxy covering with slowly elevated sides. The central part is somewhat concaved and the marginal part dull toothed. Stab culture: On " Koji "-extract gelatine (30 days at 15° C.) it forms waxy, feeble lustered, brownish, elevated isles at the mouth of the stab canal, and rosary-like colonies with gas bubbles along the canal. (b) Fluid culture: This species grows in many fluid media. According to the appearance of its fermentation it belongs to the so-called bottom yeasts. In " Koji "-extract culture (at 25° C.) yeast ring appears first after 3 days, but it does not form any complete ring even after 6 months while the sedimental yeast crop becomes somewhat plenty after 3 weeks Its development in wort or hopped wort seems to be inferior to that in " Koji "-extract. Its resisting power against Nacl is so striking that it can grow tolerably in " Koji "-extract or wort containing 20% Nacl.

III. BEHAVIOUR TOWARDS SUGARS. It was determined with Lindner's method. This species ferments dextrose, leavulose, manuose, saccharose, maltose, but not galactose, lactose, raffinose, ∝ -methyl-blucosid.

IV. FORMATION and GERMINATION of SPORE. This species is one of easily sporulable kinds among all the Zygosaccharomyces isolated from " Shoju-Moromi." This yeast does not form spores on gypsum-block at all. Sporulated cells occur very rarely in yeast ring developed in " Koji "-extract culture (3-6 months at 20° C.) or on Gorodkowa's agar medium (20 days at 25° C.). On the other hand, following the diluted " Shoju "-culture which has been described in the preceding page large numbers of ascus easily occur in the yeast ring within 7-15 days. The processes of formation and germination of spores are similar to those of Zygosaccharomyces soja which have been already described. Spores are transparent, round or oval, commonly 3-4.5 u. A few tiny grains are contained in each spore. Total number of spores in each ascus is 1-4, but the number of spores which occurs in each part is very different.

V. AFFINITY. This species seems to be nearly similar to Torula " Shoju " var. minuta which was isolated from " Shoju-Moromi " by J. Nichimura. It is necessary to ascertain the sporulation of the latter yeast after our method.   .

This yeast differs distinctly from Zygosaccharomyces soja and asporogenic species of Zygosaccharomyces by the following characteristics:

This species ferments saccharose, and the time required for sporulation of this yeast is far shorter, and the number of sporagenic cells in yeast ring is always abundant.

Zygosaccharomyces salsus distinguishes itself from this yeast by the formation of a particular film.

As far as we learn, there are seven species of Zygosaccharomyces as follows:

- (a)   Zygosaccharomyces Barkeri, Saccardow and Sydow.[1]
- (b)   Zygosaccharomyces priorianus, Kloecker.[2]
- (c)   Zygosaccharomyces javanicus, Kruyff.[3]
- (d)   Zygosaccharomyces lactis $\propto$, Dombrowski.[4]

[1]Handbuch d. Tech. Mykol. Lafer. IV. 182.
[2]Ibid.
[3]Centralbl f. Bak. II Abt. XXI 619.
[4]Centralbl. f. Bak. II Abt. XXVIII 371.

  (e)   Zygosaccharomyces japanicus, Saito.[1]
  (f)   Zygosaccharomyces fusoriens, Saito.[2]
  (g)   Zygosaccharomyces from cacao.[3]

Only the characteristic points by which these species differ from Zygosaccharomyces major will be given in the following lines:

  (a)   The cells of Zygosaccharomyces Bareri are oval and large, and sporulate on gypsum block, on several solid media containing wort or " Koji "-extract and on damp-bread, potatoes, etc., further it does not ferment maltose.

  (b)   Zygosaccharomyces prioranus forms cells of various shapes in young wort culture, and large numbers of ascus on the surface of wort-gelatine, on sterilised carrot slices, and on gypsum block, that have been immersed in wort instead of water. Moreover this species does not ferment saccharose.

  (c)   The cells of Zygosaccharomyces javanicus are oval, and this species ferments galactose, and forms large numbers of sporulated cells on agar at 26° C.

  (d)   Zygosaccharomyces lactis ∞ forms spores easily, further it ferments lactose but not maltose.

  (e)   Zygosaccharomyces japonicus produces immediately a greyish film on the surface of some nutrient fluids, and does not ferment saccharose.

  (f)   Zygosaccharomyces fusoriens does not ferment saccharose.

  (g)   Zygosaccharomyces from cacao does also not ferment saccharose.

According to the above distinctions this yeast is surely a distinct new species and we give it the name of Zygosaccharomyces major.

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[1] Centralbl. f. Bak. II Abt. XVII, XXVI.
[2] Woch. f. Brau. 1911 Nr 6. Lindner.
[3] Ibid.

II. Zygosaccharomyces soja, nov. spec.   (Saccharomyces soja, Saito[?]).

This yeast was mostly isolated from " Shoju-Moromi " which was at a young stage of the ripening process, and seems to be an important species for " Shoju "-manufacture.   Excepting the fermentability of galactose Saccharomyces soja seems to be similar to this yeast.   Moreover, there is not a great difference between Torula " Shoju " and this yeast.   According to Saito's illustration it is questionable that he, who gave the name of Zygosaccharomyces japonicus to this " Shoju "-film-yeast, comprised his " Shoju "-yeast into the genus of Saccharomyces.

Also Joergensen[1] has the same inference about this question.

I. FORM AND SIZE.   Young cells from " Koji "-extract or wort-culture (5 days at 20° C.) are commonly spherical or oval, 3.5-8 u in diameter.   The contents are homogeneous and exhibit sometimes vacuoles, and are rich in glycogen.   The cells of old cultures (after 2-6 months) in " Koji "-extract or wort are already described and are almost the same as in Zygosaccharomyces major.

II. GROWTH.   (a) Solid culture: On " Koji "-extract-gelatine-plate this yeast forms bright pearly, greyish white, mostly round and elevated colonies.   Streak culture: (1) " Koji "-extract agar (at 27 ° C.): This species forms a greyish white, waxy, elevated surface, but after a month it becomes somewhat brownish and the centre of the growth flat.   The marginal part shows tooth-like engravings.   (2) Glucose-" Sake "-agar: The growth shows yellowish white, waxy lustre, and forms an elevated smooth surface with fine streaming along the track.   The marginal part is somewhat uneven.   Stab-culture: The growth is the same as with the preceding species, but the surface of the isle is more concentrial.   (b) Fluid culture: Appearance of development of this species is very similar to that of Zygosaccharomyces major. This species can also reproduce and ferment in every nutrient fluid which contains 20% Nacl.

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[1]Die Micro organismen d. Gaerungs industrie IV Aufl. Joergensen 370.

III. Behaviour Towards Sugars. This yeast ferments dextrose, leavulose, maltose, manuose, but not saccharose, raffinose, galactose, lactose, ∞ -methyl-glucosid.

IV. Formation and Germination of Spore. On these relations we have already written fully. Form and size of spores of this species are similar to those of Zygosaccharomyces major, but the numbers of sporagenic cells are always less than in the latter species. Moreover the time required for the occurrence of sporulation is longer than that of Zygosaccharomyces major.

V. Affinity. This species does not ferment Saccharose but Zygosaccharomyces major attacks the same sugar well and both species are easily distinguished from each other by dimensions of the cells and the growths on glucose-" Sake "-agar.

This species differs from Zygosaccharomyces Barkeri by the sporogenic point of view and the behaviour toward maltose, and from Zygosaccharomyces priorianus by the cell forms of young culture and the circumstance of sporulation. Zygosaccharomyces javanicus is easily distinguished from our yeast by the size of cell and the fermentability of galactose and the formation of large numbers of spores on agar. Zygosaccharomyces lactis ∞ ferments lactose but not maltose. Zygosaccharomyces japanicus produces easily a particular film on the surface of nutrient fluid. Both Zygosaccharomyces fusoriens and Zygosaccharomyces[1] from cacao do not ferment saccharose as our yeast, but both species ferment dextrine strongly.

On the other hand, Saccharomyces soja and Torula " Shoju " seem to stand in close relation with our yeast, however, it might be appropriate to comprise together these three yeasts into one and the same species. Be that as it may, we will give it the name of Zygosaccharomyces soja.

III. Asporogenic species of Zygosaccharomyces (?).

We have hardly ever met with this yeast in our investigation. On the mycological relations this yeast is nearly similar to Zygosaccharomyces soja. This yeast forms well defined yeast

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[1]There is nothing reported about both yeasts and their behaviours towards sugars, so we will disregard both yeasts in this case too.

ring in " Shoju " and " Koji "-extract, but the sporulated cells have never been occurred in any yeast ring in spite of the presence of a number of dumb-bell-shaped cells.

According to this, this yeast seems to be a variety of Zygosaccharomyces soja which has lost the capacity of forming spores. Subsequently we have continued to cultivate this yeast in various nutrient media for restoring of the power of sporogenation. Whether this yeast has lost the faculty of producing spores transitory or constantly will be reported afterward.

B. FILM FORMING ZYGOSACCHAROMYCES

I. Zygosaccharomyces japonicus, Saito.

This species was isolated from many samples, especially from all the samples of Hamaguchi's factory. Since this yeast and Zygosaccharomyces salsus develop and form particular greyish brown films even on a concentrated " Shoju " which any other kinds of film forming yeast could no more grow, both these yeasts are the most feared ones on storing of " Shoju." Moreover this species forms a large number of sporulated cells with the greatest easiness.

I. FORMS AND SIZE. Young cells from the surface cultures on " Koji "-extract agar are round (commonly 4-8 c.c.) or oval, and contain glycogen. In old cultures club-shaped or mycerial cells are often observed. Most of the cells in a diluted " Shoju " are elongated abnormally and increase the number of vacuoles.

II. GROWTH. Solid culture: On plate-culture of wort-gelatine it forms greyish white, crater-like, elevated colony with smooth periphery, and the colour turns brownish after the lapse. of time.   Streak culture: On " Koji "-extract-gelatine: The growth shows a greyish white, somewhat dried, lustered, folded covering with fine toothed margin.   Fluid culture: " Koji "-extract culture (at 23° C.): It forms mealy white, small filmy fragments on the surface, and covers the whole surface after 3 days. The film crinkles like crepe paper increasing its thickness, and its colour changed into yellowish brown. After 3 weeks the film falls down gradually and deposits a great deal of sediment on the bottom, leaving a thin film over the surface, and at last

only a few parts of the yeast ring remain along the wall. Wort culture (at 23° C.): In the culture which was kept for 7 days film is not yet formed although gas bubbles ascend through the medium. After 3 months well defined yeast ring and thin film become observable, but this film has never been folded at all. This species reproduces and forms its particular film even in " Koji "-extract or " Shoju " which contains 23% of Nacl.

It is most noticeable that this species forms a greyish-brown, folded film on the surface of sterilised " Shoju "[30] after a long time, while other races which we isolated from " Shoju-Moromi " cease the reproduction of their cells in the same medium.

III. BEHAVIOUR TOWARDS SUGARS. This species ferments dextrose, maltose, leavulose, but not saccharose, lactose, raffinose, ∞ -methyl-glucosid, galactose.

IV. FORMATION AND GERMINATION OF SPORE. This species rarely produces spores in yeast ring of " Koji "-extract culture (after 3 months). After Gorodkowa's method sporulation occurs often after 10 days at 28° C. Following the diluted "Shoju " method which has been described in the preceding page a large number of sporulated cells occur in yeast ring after 4-5 days. Spore has somewhat thick wand and contains a few tiny grains and it is transparent, round or oval and 2.5-6 u. in size. The processes of formation and germination of spore of this yeast, and other relations are also similar to the preceding yeasts.

V. AFFINITY. This yeast seems to be identical with Zygo-saccharomyces japonicus, Saito.

II. *Zygosaccharomyces Salsus, nov. spec.*

This species was discovered in the samples taken from all the factories at Tatsuna.

I. FORM AND SIZE. Young cells from the surface culture on " Koji "-extract agar are mostly round (4-8 m) or rarely oval. The contents are homogeneous and exhibit sometimes vacuole.

II. GROWTH. Solid culture: Streak culture (27° C.): The growth shows a greyish white, feeble, finely folded covering with somewhat steepy sides. Glucose-" Sake "-agar (10 days at 25° C.): It forms a greyish yellow, folded, steepy elevated cover-

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ing with streamy margin.   Fluid culture: " Koji "-extract culture (at 23° C.): It forms a few parts of yeast ring without clouding the fluid after 3 days.   The ring grows gradually and increases its thickness.   After 3 weeks a thin film covers the surface.   The culture medium which was kept for 3 months has been decolourised strikingly.

Wort culture is similar to the former culture.   But this yeast forms a greyish white, folded, thick film on " Shoju " or " Koji "-extract which contains a quantity of Nacl.   This yeast is easily distinguished from Zygosaccharomyces japonicus by this characteristic point.

III.   BEHAVIOUR TOWARDS SUGARS.   This species ferments dextrose, leavulose, maltose, but not galactose, lactose, saccharose, raffinose, $\propto$ -methyl-glucosid.

IV.   FORMATION AND GERMINATION OF SPORE.   In these relations this yeast is similar to Zygosaccharomyces japonicus, but the time required for sporulation of this yeast is longer than that of the former species.

V.   AFFINITY.   This yeast forms a fold thick film in some nutrient fluids which contain a quantity of Nacl, but not in the absence of Nacl.   Moreover this yeast is easily distinguished from the former species by the cell forms[1], and the time limit of sporulation.

Torula soja G. and H. Nishimura[2] seem to be identical with this species.   From above differentiation we gave it the name of Zygosaccharomyces salsus.

SUMMARY.

1.   It is a very interesting fact that five different species of Zygosaccharomyces were isolated from " Shoju-Moromi."

2.   Zygosaccharomyces major was mostly isolated from the samples of mature stage while Zygosaccharomyces soja from the samples of young stage of the ripening process.   There is no doubt that these two Zygosaccharomyces play an important rôle in the ripening of " Shoju."

[1] Film cells of Zygosaccharomyces japanicus is always more or less prolonged.
[2] Nōgaku Kwai hō.

3. Zygosaccharomyces japonicus and Zygosaccharomyces salsus easily produce greyish white, crepe-paper-like films even on a concentrated " Shoju " which any other kinds of film-forming yeast could no more grow. Moreover these two yeasts form a large number of sporulated cells with great easiness. They are therefore most fearful ones on storing of " Shoju."

4. It is probable that specific differentiations of " Shoju " yeasts which have been studied by several authors, have not coincided with one another owing to their sporulating difficulties.

5. If it be desired to observe the spore formation of " Shoju " yeast it should be undertaken in the following ways:

The yeast is sowed in a sterilised test tube which contains a quantity of diluted " Shoju " diluted with water to make its salt-content 5%, and the culture is laid at 28° C. for the first 3 days and then immediately kept at 20°-25° C. for 7-15 days.

SOME CHARACTERISTICS OF AMERICAN WINES

(Produced in the Eastern States)

By Lee J. Vance

New York, N. Y.

In order to understand and appreciate the leading types or kinds of American wines, it is necessary to know something about the different grapes from which these wines are made. Thus, a brief notice of American viticulture will prepare the way for a study of American wines.

The grape growing industry of the United States presents certain interesting and important features. It is unique in two respects.

In the first place, there is no grape and wine growing country in the world with such a wide range of climates and soils as you find in the United States. Here, it is possible to grow, and there are grown almost all of the well-known wines of France, of Italy, of Spain, of Portugal, of Germany, and of Austria-Hungary. The result is that in the United States are made almost all of the wines typical of the countries just mentioned. And so we have American dry red wines like the clarets and Burgundies of France, and the Chiantis of Italy. We have American dry white wines like the Sauternes of France and the Hocks of Germany. We have American sparkling wines like the champagnes of France and the sparkling wines of Germany and Italy. We have, finally, American sweet wines like the Ports of Portugal, and the sherries of Spain.

In the second place, there is no grape and wine growing country in the world with such widely different species of vines as you find in the United States. In Europe, all of the different wines are made from a single species of grape, the Vitis Vinifera. In the United States, all of the different wines are made not only

from vinifera varieties, but from several distinct species of native or American grapes.

Therefore, American wines fall into two broad classes:

1.   Wines which are made from Vinifera or European varieties of grapes.

2.   Wines which are made from the native or American grapes.

All of the grapes grown in the United States east of the Rocky Mountains are native varieties.   The wines from these grapes are commonly designated as " Eastern Wines."

All of the grapes grown west of the Rocky Mountains are of the vinifera or foreign varieties.   As practically all of the wines from these grapes are produced in California they are known as "California Wines."

About Eastern Wines

The development of our native grapes forms a most interesting chapter in the history of American viticulture.   For a period of just 200 years—that is to say, beginning in 1619, when the London Company at the solicitation of Lord Delaware sent a number of French vignerons with a collection of European varieties of grapes to Virginia, down to the year 1819, when Major John Adlum found and introduced the first superior variety of an American grape which he called the " Catawba "—every attempt to establish vineyards of vinifera or European grapes in the Eastern States resulted in loss and failure.

Finally, when it was evident that the European varieties of grapes would not thrive outdoors in the Eastern States, our enterprising horticulturists turned their attention and effort to the native grapes, which they found growing wild and practically neglected and uncultivated.   They gradually succeeded in obtaining some improved varieties, and, as the result of their patient work, have come the best and most popular American grapes of to-day, such as Catawba, Delaware, Concord, Isabella, Rogers Seedlings, Ives, Norton etc.   Some of our most valuable native varieties are purebred seedlings, while others are hybrids between the European and American grapes.

American grapes do not belong to a single species of the vine, as do the European grapes.   Prof. L. H. Bailey, an authority

on this subject, has defined or classified no less than 23 species of American grapes, but only half a dozen have been cultivated to any extent.

The *Vitis Labrusca* was the first species of American grapes to be improved. The Catawba, the first American grape of quality, is a Labrusca, but it shows some vinifera or foreign blood. The same thing is true of the Isabella, which was introduced and became popular about the same time. Two of our finest grapes, both for the table and for wine—the Delaware and Iona—are of Labrusca parentage, but with a strain of vinifera blood.

Although there are several hundred varieties of American grapes, only some 20 or 25 kinds have been or are used to any extent for making wines. The varieties for wines are:

Bacchus, Catawba, Clinton, Concord, Cynthiana, Delaware, Diamond, Diana, Dutchess, Elvira, Eumelan, Goethe, Herbemont, Iona, Isabella, Ives, Lenoir, Montefiore, Missouri, Riesling, Niagara, Norton, Noah, Othello, Rommel, Scuppernong, and Taylor.

There are a number of excellent varieties of American grapes that have never been developed as they should be, and consequently they are still cultivated on a small scale.

The following is a short table of Eastern Wines and the principal varieties of grapes used in making them:

RED DRY WINES (Claret and Burgundy types)—Ives, Norton, Clinton, Concord, Cynthiana, Eumelan, etc.

WHITE DRY WINES (Rhine and Sauterne types)—Catawba, Delaware, Iona, Missouri, Reisling, etc.

SPARKLING WINES (Champagne)—Delaware, Catawba, Dutchess, Diamond, Bacchus, etc.

SWEET WINES—Catawba, Isabella, Iona, Scuppernong, etc.

The leading grape and wine growing in Eastern States are: New York with 60,000 acres of vines and an average annual production of from 4,000,000 to 5,000,000 gallons of wine; Ohio with about 8,000 acres of vineyard and an average annual production of 3,000,000 to 4,000,000 gallons of wine; Missouri with about 4,500 acres of vines and an average annual production of about 2,000,000 gallons; Michigan with about 12,000 acres of vineyard and an average annual production of 1,000,000 gallons of wine.

The States of New Jersey, Virginia, and North Carolina have about 2,000 acres of vines and an average annual production of about 250,000 gallons of wine in each State.

The Eastern wine industry is still in the early stages of its development. It was really established only about fifty years ago by Hon. Nicholas Longworth at Cincinnati, O. Since then, wine making extended to other places, and, considering the difficulties including the unreasonable opposition of the prohibition agitators, the industry has made good progress.

The more marked characteristics of our native grapes are naturally reflected in our native wines. In some respects these wines are in a class by themselves, They are like and yet unlike foreign wines, which, in turn, differ greatly from each other.

The characteristics of wines are revealed first, by the senses, and secondly, by chemical analysis.

The senses, when at all keen or cultivated are quick to detect certain peculiarities of a wine. The eye sees if a wine has good color, if it is clear or cloudy, if it is bright or dull; the tongue tells us if the wine is sound or diseased, if the taste is pleasant or disagreeable, if it is smooth or harsh; the nose recognizes if the wine has an odor or any aroma, and if it has even a faint or delicate bouquet.

A chemical analysis discloses certain other characteristics. It shows the alcoholic strength of a wine, its sugar content, the percentage of extract, the different acids and the total acidity — in brief, it shows the composition of a wine. The results which are obtained in the analyses of wines furnish valuable data for determining their purity and their quality, and from this data standards can be and are formulated for passing upon wines in the same class. These standards are useful in judging wines from the same country or the same district, although they may not be entirely correct for wines from other countries and other districts. Therefore, as might be expected, owing to widely different varieties of grapes, climates, soils, locations, and methods of vinification Eastern wines vary greatly in character among themselves and from California wines, while both differ from foreign wines of the same kind or type.

The first characteristic of native grapes and American wines

was described by the word "foxy." It referred to their pronounced taste and smell. Just why this word was used is uncertain. According to Prof. Bailey, " several explanations have been given of the origin of the name fox-grape, some supposing that it came from a belief that foxes eat grapes, others that the odor of the grapes suggests that of the fox. I am inclined to suggest " he adds, " that the name may have originated from the lively foxing or intoxicating qualities of the poor wine which was made from the wild grapes. At the present day we speak of ' foxiness ' when we wish to recall the musk-like flavor of the wild Vitis labrusca; but this use of the term is of later origin, and was suggested by the name of the grape."[1]

It is not easy to define a flavor, and so the word " foxy " does not correctly describe the characteristic taste and aroma of many American wines. Some of these wines are not " foxy " at all. Some of them might be called " musky," while other native wines have a balsamic flavor and aroma. The early foreign critics who were familiar only with the commonest varieties of American grapes and the poorer qualities of American wines, used the word " foxy " to condemn them, but it simply showed that they did not like the grapes or the wine.

The old saying is, " Everyone to his taste." People differ very much in their tastes, and what suits one person may not suit another. Some of the European grapes are flat and insipid, and some of them are disagreeable to the American palate in their astringency. Consequently the wine from such grapes have little character and they do not make a pleasant drink and yet they are the popular beverages in the places where they are produced.

It is an interesting fact that, people generally like the wines of their own district and their own country better than the wines of another district and another country. This is true not only of grapes and wines, but of many other products. It is not a question of quality or price, but simply a matter of taste. Every season the American people eat immense quantities of their native grapes, such as the Delaware, Concord, and Catawba; they like their flavor and aroma, and naturally they appreciate the same quantities in the wines made from those grapes.

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[1]Evolution of Our Native Fruits, p. 5.

The same thing is found in the wine growing countries of Europe where the wines of each district have a local reputation. Thus, the people of Italy, of France, of Germany, of Spain, and of Austria-Hungary prefer their own wines. Even the people of the different districts in those countries usually think their wines are better than those of other districts.   For example, take an Italian away from home and in a foreign country. You may offer him a wine which you think is better than his native kind, but you will find that he prefers an Italian wine, and, if he cannot get it, he wants a wine very similar in taste and character to the vintages of his native place or land.

With the introduction of millions of American vines in European vineyards this question of the character and composition of American wines have received an added interest. In the decade from 1870 to 1880 the vineyards of France were threatened with utter ruin by phylloxera, but they have been saved by the use of American vines. It was found that our native grapes, as the result of natural selection, have become more or less resistant to the attacks of phylloxera. First in point of resistance are the wild vines of our Southern and Southwestern States, and hence they furnish what are called the " resistant stocks," Thus, the vineyards of France have been and are being replanted or reconstituted by American vines of two kinds: (a) those known as direct producers, and (b) those used as stocks on which are grafted the non-resistant or European varieties of grapes.

Now, there is a wide difference of opinion as to just how much and in what way American vines in Europe have influenced the character or quality of the wines. As might be expected, wines from direct producers retain more or less the so-called "foxy" taste, and some of the fine varieties of American grapes which make excellent wines in this country have given poor results in France. This is due, of course, to the difference in climates, soils, and locations, etc. The same result is found when even the choicest French wine grapes are grown in other countries, as, for example, the Cabernet Sauvignon, from which the finest claret of the Medoc is made, produces the poorest kind of a wine in Algeria.

As to the wines made from the French-American hybrids and from grapes grown on American or resistant stocks, they also

show influences of their origin. It could hardly be otherwise. On this point M. Jamain in his work on "La Vigne et Le Vin" says:

It must be admitted that this vigor of hybrids in general is shown particularly when the American vine plays the rôle of the female or mother. That is to say, if we wish to give to the hybrid strong vegetation or growth and resistance to phylloxera, this growth and this resistance should be taken from the female element in the American vine selected to fertilize the plant. But if we want high flavor, abundance of fruit, and all those qualities that characterize our own vines, they will be transmitted to the hybrid when a French stock plays the rôle of the male or father. On the other hand, there is much less chance of quality and quantity from the hybrids if in the crossing, an American stock furnished the fertilizing pollen.[1]

Similar opinion are set forth in the reports presented to the Congress on Hybridization of the Vine, which was held in Lyon, France, in 1901.

Briefly stated, many French viticulturists claim it is a general law that the mother transmits more of vine or tree characteristics while the male, or pollen parent, transmits more of the fruit characteristics.

This conclusion is not accepted by some of our best authorities. Prof. T. V. Munson, of Denison, Texas, a man who has spent a lifetime in the study of hybridization, and who has originated many hybrids, is skeptical about the law just quoted. He says:

After observing and studying my crosses and hybrids with reference to this point, there seems to be no adequate ground of support to lay it down as a law, farther than that the mother appears to transmit its degree of hardiness in resisting climatic extremes and diseases better than the male parent. Theoretically this would be reasonable, as the ovule, after impregnation, receives all of its support and growth from its mother, until it becomes a mature seed, hence the mother vine should always have the greatest capability possible to endure hardships and resist disease and yet include excellence in fruit.[2]

[1]La Vigne et Le Vin, par Paul Jamain, p. 144.
[2]Foundations of American Grape Culture, p. 138.

The significance of these studies has been recognized by French viticulturists, many of whom from patriotic or commercial reasons are reluctant to admit that American hybrids and resistant stocks have modified the character or quality of their well-known wines. This was shown when Prof. Lucien Daniel, professor of botany in the University of Rennes made a report in which he held that American vines had a bad effect on the quality of French wines. He said:

The grafting stock alone, combined with more intensive culture, was responsible to a great extent for the bad results, namely, large quantities of inferior wine, a lowering of the resistance to external conditions. and modification more or less profound, but sure of the French vine stocks.

Again, in 1907, Prof. Daniel was appointed by the French Minister of Agriculture to investigate the vineyards of the South of France. In his report he claimed that the growers of the Midi had sacrificed quality for quantity, because they could obtain large yields from resistant vines. He alleged that in taste and quality the wines of recent years are inferior to the wines of former years. He pointed to the differences shown by the chemical analysis of wines from the old stocks.

Some of the French critics of Prof. Daniel have gone to the other extreme in denying any influence of American vines on the character or quality of their wines. Others in their arguments have claimed that there has been an improvement in the quality of the wine. M. Jean Dupuy, ex-Minister of Agriculture and President of the Society of Viticulteurs, in his reply to Prof. Daniel says that the composition of the wines from grafted stocks are about the same, and in some cases are superior. "Their conservation is better," he adds, "because of improved methods of vinification."[1]

In their standard work, " Les Vignes Americaines " Professors Viala and Ravaz, both of whom are high authorities, hold that wines produced from grafted vines are equal and often superior quality particularly in alcoholic strength, to those produced by the same varieties when not grafted. They say:

[1]Bulletin de la Societe des Viticulteurs de France. 1907. p. 178.

Numerous comparisons that have been made in the vine-
yards of producing fine wines (Burgundy, Beaujolais, and Medoc)
have fully proved that the quality of the wine from grafted vines
is equal, if not superior to that from non-grafted vines.   It is
evident that in order to arrive at a correct deduction in the com-
parison, the fact that the old vines give wine of a superior quality
to young vines must be taken into account.   Conclusions on this
point are only of value when the wines compared have been made
from vines of equal age, the same variety, grown in similar soils,
and submitted to the same methods of culture.[1]

The American grapes planted somewhat extensively in France
during the early period of the phylloxera were very ordinary and
inferior kinds.   These included such varieities, as Othello,
Jacquez, Black-July, Canada, Cornucopia, Solonis, York,
Madeira—varieties considered of little worth in this country and
hardly ever used by our wine makers.   Later a number of grapes
of better and higher quality were introduced.   Some, like the
Delaware, Catawba and Norton, proved to be non-resistant and
had, therefore, to be given up.   Others, like the Clinton, Cynthi-
ana, Herbemont, and Noah are of fair quality and are still grown
in France for wine.

The Jacquez, sometimes called the Lenoir, is cultivated with
success in many departments of France.   M. de Dubor says the
Jacquez has been regarded for many years in the South of France
as a direct producer of the highest merit.[2]

Prof. Rougier in his manual on wine making says the wine from
Jacquez grapes has a fresh taste, a good body and constitution, is
sufficiently alcoholic, and has a very deep color.[3]   It, therefore,
makes a good blending wine.   One trouble is that continued expos-
ure to the air affects both the color and taste.

Another very ordinary grape is Othello which does not amount
to much here.   It does well in France, and M. Sabatier declares
Othello wines the best of American wines—an opinion which will
surprise our wine makers.   This wine is described as having good

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[1]American Vines, By P. Vialla and L. Ravaz.   Translated by R. Dubois and
E. H. Twight, p. 207.

[2]Viticulture Moderne, par G. de Dubor.

[3]Manuel de Vinification, par L. Rongier, p. 114.

vinous qualities, from 10 to 11.5 degrees of alcoholic strength and a bright red color. The foxy taste is said to largely disappear in aging.

Dr. Cazalis in his book on the " Art of Wine Making " has a chapter devoted to the vinification of grapes from American stocks. Besides Jacquez and Othello, he discusses the qualities of the wines from Clinton, Cynthiana, Cunningham, and Herbemont. Dr. Cazalis agrees with many of our wine makers regarding the excellent qualitites of Cynthiana. He mentions having first drank this wine with great pleasure at a banquet of the Central Agricultural Society of Herault, and says it had many of the quanities of a fine Burgundy.[1]

The differences in composition between wines from American grapes and those from French grapes on American stocks are revealed by chemical analysis. One of the early contributions to this phase of the subject was made by Prof. Bouffard, who published in 1890 a table giving the analyses of 38 samples of wines from American grapes grown in France and of 9 samples of wines from French grapes grafted on American stocks.

For the purposes of comparison the analytical results may be condensed as follows:

1. *Wines from American Vines*—Alcoholic strength averaged 10.99 deg. with a minimun of 7.5 and a maximum of 14.30.

Acidity averaged 4.82 per mille, with a minimum of 3.04 and a maximum of 6.75.

Dry extract averaged 25.72 per mille, with a minimum of 14.8 and a maximum of 39.50.

II. *Wines from French Vines.*—Alcoholic strength averaged 8.33 deg. with a minimum of 6.60 and a maximum of 10.20.

Acidity averaged 5.17 per mille, with a minimum of 4.64 and a maximum of 6.13.

Dry extract averaged 20.92 per mille, with a minimum of 17.30 and a maximum of 22.80.

Hence, the wines from American varieties of grapes were on the average more alcoholic, less acid, and richer in dry extract than the wines from French grapes on American stocks.

[1]L'Art de Faire Le Vin, par Dr. F. Cazalis, p. 392.

This conclusion need some explanation; that is to say, it would not hold good if we compared wines made from grapes grown in the Eastern States with the same class of French wines. In that case, the correct statement would be that our Eastern wines are on the average less alcoholic, more acid, and richer in dry extract than the French wines from grapes on either resistant or non-resistant vines.

Unfortunately, for purposes of comparison, the 38 samples analyzed by Prof. Boufford did not include a single wine from varieties of grapes which are used at the present time in making the well-known Eastern wines, both dry and sparkling. But we may draw two conclusions:

First, that the quality of American grapes changed considerably when grown in France; Second, that the character of the French wine was modified by the American wines.

Some data on this point may be found in the report of Dr. Joseph Boussingault on the wines at the Paris Exposition of 1878. It gives the analyses of 1,000 French wines and of 15 American wines, all Eastern wines. As this is one of the earliest examinations of Eastern wines made by an expert wine chemist, some of the results may be noted.

The following shows the composition of a Catawba wine made in Virginia:

	Per Litre	
Density	0.994	
Alcohol (by volume)	133.0	c.c.
Total Acidity (as SO$_4$HO)	4.593	Gr.
Cream Tartar	0.256	Gr.
Glucose	0.5	Gr.
Dry Extract	38.7	Gr.
Glycerine	10.0	Gr.
Succinic Acid	2.00	Gr.
Ash	1.5	Gr.

Compare this with a Catawba wine made in Missouri labeled " first quality " at the same exposition:

	Per Litre	
Density	0.999	
Alcohol (by volume)	119.0	c.c.
Total Acidity (as SO_3HO)	5.218	gr.
Cream Tartar	0.256	gr.
Glucose	10.7	gr.
Tannin	0.037	gr.
Dry Extract	40.8	gr.
Glycerine	10.2	gr.
Succinic acid	2.04	gr.
Ash	3.5	gr.

The following analysis is of a New York State sparkling wine produced by the champagne process, an industry which was in its early stages in 1878:

	Per Litre	
Density	1.024	
Alcohol (by volume)	128.0	c.c.
Total Acidity (as SO_3HO)	4.860	gr.
Cream Tartar	0 262	gr.
Glucose	64.2	gr.
Dry Extract	111.5	gr.
Glycerine	8.9	gr.
Succinic acid	1.78	gr.
Ash	1.0	gr.

Compare this with the following analysis of a New York State champagne coming from the same district at the Paris Exposition of 1900:

Specific Gravity	1.0042
Alcohol (by volume)	13.79
	Grams per 100 c.c.
Alcohol	10.87
Glyceral	.7330
Extract	5.63
Ash	.128
Total acids	.693
Total Tartaric Acid	.280
Tannin	.032

In the Bulletin of the U. S. Bureau of Chemistry on American Wines at the Paris Exposition of 1900, analyses of 63 samples of wines are presented. Sixteen of these analyses show the composition of Eastern wines. It would be interesting to compare, if time permitted, the improved quality and character of Eastern wines of recent date over wines produced twenty-five or thirty years ago. This improvement is due to more knowledge of the qualities of different grapes, to greater care in the selection of the fruit, and better methods of vinification.

It is to be regretted that the analytical data for a thorough study of American wines produced both in the Eastern States and in California are at present so meagre and incomplete. Dr. W. D. Bigelow has made a beginning by compiling the results of 845 analyses which were made by different persons and at different times.[1] Only 132 analyses are given of Eastern wines. Commenting on the data which he gathered, Dr. Bigelow says:

The volume of work which has been done is not sufficient to justify the adoption of standards for American wines. It appears that our wines differ to some extent from those of other countries but we are not yet able to determine just how great those differences are. It seems important, therefore, that the musts and wines from all the wine producing sections of the country should be examined.

The necessary work along this line is now being conducted by Prof. W. B. Alwood, of the Bureau of Chemistry. He has started by making a detailed study of the composition of the grapes used for wine making, more particularly in New York, Ohio, and Virginia. Referring to the qualities shown by certain wine grapes grown in New York and Ohio, Prof. Alwood says:

The Delaware and Iona have a remarkably high sugar and low acid content; Catawba shows a fairly high sugar and also high acid; the Ives and Concord are low in acid and not sufficiently high in sugar to make a claret wine of usual strength. Clinton and Norton can be grown with sufficient sugar content to make a fine, sound wine, but they are strongly acid.[2]

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[1]The Composition of American wines. By W. D. Bigelow. Bulletin No. 59 Bureau of Chemistry. 1900.

[2]Enological Studies, By W. B. Alwood, Bulletin No. 140 and 145. Bureau of Chemistry. 1911.

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The samples of Delaware and Norton grown in Virginia showed their splendid qualities for making fine wine. In the two seasons of 1909 and 1910 the Delaware averaged about 21.5 per cent. sugar, and about 6.5 per mille acid. The Nortons for three years averaged above 22 per cent. sugar and about 8 per mille acid.

To sum up: three natural characteristics of Eastern wines stand out. They are: 1. A pronounced flavor and aroma. 2. A very moderate alcoholic strength. 3. A rather high acidity.

(1) As to the first named characteristics of American wines—flavor and aroma—they come from the kind of grapes used. There is a great difference in the vinous character of grapes.

Certain varieties, such as Concord and Ives which make fair dry red wines, give what has already been described as a "foxy taste." Some people call it a "grapey taste" and rather like it. In my opinion, and to my palate, the foxy taste in American wines is no worse than the disagreeable flavors and odors which I have found in some Spanish wines, in some Italian wines, and in some Algerian and French wines. However, in order to satisfy the demands of their clientele the expert foreign wine makers by proper handling of the must and careful cellar treatment are able to remove wholly or partially the taste in wines made from those varieties of American grapes that have the foxy flavor or aroma.

On the other hand, certain American wines have a flavor and aroma that wine experts and connoisseurs recognize as something very desirable. Thus, a Norton's wine will often carry the delicate raspberry flavor so highly prized in certain *grand vins* of the Médoc and of Burgundy. I have tasted a fine old Delaware wine that conveyed the impression of the strawberry, and when the bottle was opened the aroma was equal to that which comes from the celebrated Cabinet wines of the Rhine and the Moselle. A Catawba wine of a good year, properly made and handled, will have fine flavor, freshness, and delicate character; and so an Iona wine will sometimes reveal a pleasant musky taste or a banana-like flavor. As a general rule our Eastern wines which are produced in the temperate climates of New Jersey, New York, and Ohio require several years both in cask and in bottle before they develop their final or best qualities.

(2) As to the moderate alcoholic strength of Eastern wines, this is due to the climate and the composition of the grapes. In Virginia and the Southern States, where the seasons are long and warm, the grapes usually ripen and will yield a must that contains from 18 to 22 per cent. sugar, or say from 9 to 11 per cent. of alcohol. The climate of the wine districts of northern France and of the Rhine in Germany, is sometimes subject to bad conditions, such as a late, cold Spring, or an early cold Fall. Thus, the number of really fine vintages in Burgundy, in Champagne and on the Rhine and Moselle, is quite small, and when the season has been an exceptionally fine one the wine of that year takes the highest rank. There have been about five such vintages in the past fifty years in Germany, or one good year in ten.

On the whole the seasons in our Eastern wine districts are fairly regular, and the chances are even of obtaining a good grape crop. The sugar content of American varieties is lower on the average than that of foreign grapes, and in poor seasons there is hardly enough sugar to give a wine of proper alcoholic strength, say of 9 to 10 per cent. The addition of a small quantity of sugar to bring up the must to a normal composition is desirable in such cases, and this is recognized being just as legitimate as the addition of a small quantity of tartaric acid to the must that is deficient in acidity.

(3) As to the rather high acidity of Eastern wines, this again, comes from the climate and the composition of the grapes. The sugar and the acid content follow one another. In the hot or warm climates the grapes usually contain too much sugar and too little acid, and the wines from such grapes are seldom of high character or good lasting quality.

The acid content of American varieties averages considerably higher than that of foreign grapes, and in bad seasons there is too much acid for a good, palatable wine. In such cases it is necessary to reduce the acidity.

Prof. Roos, director of the Viticultural Station of Herault, has laid down the rule, which is now generally accepted, that all dry wines to be of good quality should contain 8.6 grammes of total acid per litre, calculated as tartaric acid. He says that all wines

udged favorably by expert wine tasters always possess a rela-
;ively high acidity which does not go below the percentage men-
;ioned.

The finest qualitites of Eastern wines—qualities which make
them stand high among the wines of the world—come when they
have a proper amount of acidity. It is the acidity that is largely
responsible for the high, bright color of the Norton's wine; for the
freshness in taste of well-made Catawba wine; for the delicate
bouquet of fine, old Delaware and Iona wines.

It is now known that the free acids help to conserve or preserve
a wine, in that they check the actions of injurious ferments. They
thus give to wines a certain vigor or "constitution," so that wines
light in acid usually mature at an early age. Such wines soon
"grow old" and after a short time they " break down " and
lose their best qualities. This is generally the fate of dry wines
produced in warm climates.

On the other hand, Eastern wines produced in the northern
or cold climates come to maturity slowly and develop their best
properties only after several years. The acids also play an impor-
tant rôle in the formation of the bouquet. Their action has not
been fully explained, owing to the complex origin of the different
fragrant ethers, the chief one being oenanthic ether.

Thus far, the best kind of Eastern wines are the dry white
varieties, such as those of the Moselle, Hock, Graves, and dry
Sauterne types.   The white wines made from the Catawba
grapes resemble in style the German Hocks, although they have of
course other characteristics of their own. Wines of the dry Sauterne
type are made from the Delaware grapes, the wines being clean and
delicate, and without the sweetness usually found in the French
Sauternes.

Of the dry red wines, the Norton, which is the best, is more
of a Burgundy type, having a splendid ruby color, plenty of
body, and a fine fruity flavor. Burgundy types can also be
made from the Cynthiana and Franklin grapes.

The most successful of the Eastern productions is its spark-
ling wine of the true champagne type.   In fact, 75 per
cent. or more of all the American Champagne is produced in
the Eastern States.   The headquarters of this sparkling wine

industry is in the Lake Keuka region of western New York, which has become known as "the American Champagne district." Certain varieties of Eastern grapes have the right acidity and neutral flavor, while other varieties give the snap, sparkle and *mousse,* so that when blended together they yield a result that corresponds to the wines from the Champagne district. Of the Claret types, there are a number of different kinds, but like the French clarets they could be improved by judicious blending.

There is no doubt that the proper blending of Eastern wines both with each other and with California wines would give good results. The whole practice of blending is based upon the differences between wines, so that the mixing together of different kinds or qualities of wines should yield a better product than any one of the wines that went into the blend. With the exception of some Château wines of France and a few Schloss wines of Germany, practically all of the well-known and popular wines of Europe are the result of careful blending. Even in the making of champagne, which in some respects represents the highest art of the wine maker, because special knowledge and skill are required, the character and quality of the final product is based upon the blend in the *cuvée.*

In this and other ways I look to see our Eastern wines improved, made more uniform, and elevated to that high standard which the fine qualities of our American grapes warrant.

ON SYMBIOTIC LIFE OF YEAST RACES

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Symbiotic phenomena between yeast races have been very little studied, despite the fact that the yeasts used in the fermentation industries are seldom pure, and generally consist of two or more different races.

In 1881, Hansen (C. R. Labor. Carlsb., 1881 1.59 Z.ges Brauw. 1881, 4,449) found that cultures of *Saccharomyces Apiculatus*, when mixed with ordinary bottom yeast, multiply less rapidly than the two species cultivated separately in nutritive wort of the same composition. In the fermentation of wine, the cells of *Saccharomyces Apiculatus* have an unfavorable influence (H. Muller-Thurgau—Koch's Jahresber.1895, 6-182) upon wine-yeast, and especially upon *Saccharomyces Ellipsoideus*, reducing the fermentation, as well as the multiplication of the cells.

Even in the cultivation of pure yeast races, antagonism toward succeeding generations is encountered; Duclaux (Traite de microbiologie, Paris—900 I and III) has found that culture wort in which a certain species of yeast is cultivated becomes from generation to generation less favorable for development, even when the same quantity of nutritive substances is present before each cultivation. On the other hand, Thibaut (Centrbl. Bakt. II, 1902—9,743) has proved that the products of fermentation when present in amounts of about 20 per cent., increase the rapidity of multiplication.

It is essential to remember that Hansen (C. R. Labor. Carlsberg, 1881—1, 59—Z ges. Brauwesen, 1881, 4,449) found antagonism in mixed cultures of *Saccharomyces Apiculatus* and common bottom yeast, and Muller-Thurgau (Koch's Jahresber. 1895,—6,182) in symbiotic cultures of *Saccharomyces Apiculatus* and wine yeast.

In industrial and spontaneous fermentations, the final result depends upon the combined actions of the symbionts; it is, how-

ever, very difficult to determine whether the result obtained—
the total action—is greater or smaller than the sum of the actions
of each race or species separately.

Interesting results may be obtained by introducing two yeast
races into the same culture fluid. For this purpose, I have in
collaboration with my assistant, Mr. L. Bosmans, compared the
phenomena of fermentation by two races mixed, with the fer-
mentation by pure races alone.

We have experimented with six yeast races:

1. Saccharomyces cerevisiae, Carlsberg, bottom yeast.
2. Saccharomyces cerevisiae, Saaz, bottom yeast
3. Saccharomyces cerevisiae, Frohberg, top yeast
4. Saccharomyces cerevisiae, Logos, top yeast
5. A yeast cultivated pure from fermenting honey; it is
   identical with *Zygosaccharomyces Priorianus* (Klocker)
   (Th. Nussbaumer—Z Unters-Nahrungsm.   1909—
   20,272-277)
6. *Schisosaccharomyces* Pombe—top yeast.

The yeast races 1, 2, 3, 4 and 6 were taken from the collection
of the Institute of Brewing of Ghent, (cultivations of Professor
L. Melard). The honey race (No. 5) was cultivated pure in the
chemical and bacteriological laboratory of the City of Ghent;
all the cultivations were made under the same conditions, and
the cultures used for inoculation were prepared in the same wort
by six days incubation at 25 C.

In the experiments with single yeast races, we employed 2 cc
of the liquid culture, while in the experiments with two races,
1 cc of each culture was used.

The culture media were prepared as follows:

A. Glucose and Peptone (56.86 grm. glucose + 20 grm.
   peptone Witte in a liter).
B. Wort (with 54 grm. Maltose in a liter).
C. Saccharose and Peptone (54 grm. Saccharose + 20 grm.
   Peptone Witte in a liter).

The fermentations were carried out in Erlenmeyer flasks of 150 cc capacity, and in each experiment we used 50 cc of the culture medium. After inoculation, the flasks were closed with *Hartmann* sulphuric acid bulbs, and weighed; the fermentations were conducted at 25 C.

From day to day, the amount of carbonic acid gas given off was determined by the loss in weight.

A. Cultures with one Same Yeast

(a) Glucose and pepton

CO_2 set free after days	1	2	3	4	7	8
S. cerevisiae Carlsberg	——	——	——	——	0	——
" Saaz	——	——	——	——	0	——
" Frohberg	0.05	0.11	0.22	0.40	0.85	0.88
" Logos	0.40	0.95	0.95	1.00	1.00	——
Zygosaccharomyces	0.07	0.30	0.45	0.52	0.60	0.62
Schizosacch. Pombe	0.23	0.78	1.03	1.08	1.08	——

(b) Wort (maltose)

CO_2 set free after days	1	2	3	4	7	11	14
S. cerevisiae Carlsberg	0.30	0.60	0.90	0.90	0.95	1.00	——
" Saaz	0.05	0.65	0.75	0.75	0.85	0.95	——
" Frohberg	0.60	0.80	0.90	0.90	0.90	——	——
" Logos	0.60	0.95	1.00	1.00	1.05	1.15	——
Zygosaccharomyces	0.15	0.30	0.50	0.65	0.95	1.05	1.10
Schizosacch. Pombe	0.40	0.95	1.05	1.10	1.20	1.25	1.35

(c) Saccharose + pepton

CO_2 set free after days	1	2	4	5	7	9	12
S. cerevisiae Carlsberg	0.05	0.15	0.40	0.70	1.10	1.15	——
" Saaz	0.07	0.40	1.15	1.30	1.30	——	——
" Frohberg	0.30	0.95	1.45	1.50	——	——	——
" Logos	0.37	1.05	1.35	1.40	1.40	——	——
Zygosaccharomyces	0.05	0.10	0.15	0.15	0.30	0.50	0.79
Schizosacch. Pombe	0.12	0.80	1.20	1.20	1.20	——	——

B. CULTURES WITH TWO MIXED YEASTS
I
Cultures with S. cerevisiae Carlsberg and another race

1°. S. Carlsberg + S. Saaz

CO₂ set free after days		1	2	3	4	5	7	9	11
(a) Glucose +	found	—	0.44	0.97	1.00	—	1.00	—	—
pepton	calculated	0	0	0	0	0	0	—	—
(b) Wort	found	0.30	0.80	0.90	0.90	—	0.95	—	1.00
(maltose)	calculated	0.17	0.62	0.82	0.82	—	0.90	—	0.97
(c) Saccharose	found	0.10	0.40	—	0.90	1.05	1.25	—	—
+ pepton	calculated	0.06	0.27	—	0.77	1.00	1.20	—	—

In these experiments, smybiosis gives valuable results and no antagonistic action is apparent. It is a curious fact that used separately, neither of these two yeasts will ferment glucose-peptone; but when mixed together, they produce active fermentation.

2°. S. Carlsberg + S. Frohberg

CO₂ set free after days		1	2	3	4	5	7	9
(a) Glucose + pepton	f.	0	0.02	0.07	0.93	—	0.93	—
	c.	0.02	0.05	0.11	0.20	—	0.42	—
(b) Wort (maltose)	f.	0.45	0.70	0.75	0.75	—	0.75	—
	c.	0.45	0.70	0.90	0.90	—	0.92	—
(c) Saccharose + pepton	f.	0.26	0.95	—	1.50	—	—	—
	c.	0.17	0.45	—	0.92	1.10	1.32	1.62

In this case a bottom yeast, Carlsberg, works with a topyeast, Frohberg.

In wort, the fermentation with mixed races, is slower than with each race alone. In glucose + pepton and saccharose + pepton the fermentation is more active. Consequently antagonism is not a general rule.

3°. S. Carlsberg + S. Logos

CO₂ set free after days		1	2	3	4	5	7	11
(a) Glucose + pepton	f.	0.37	0.94	0.98	0.98	—	1.00	—
	c.	0.20	0.47	0.47	0.50	—	0.50	—
(b) Wort (maltose)	f.	0.55	0.80	0.90	0.90	—	0.90	1.00
	c.	0.45	0.77	0.95	0.95	—	1.00	1.00
(c) Saccharose + pepton	f.	0.25	0.95	—	1.30	1.35	1.35	—
	c.	0.21	0.60	—	0.87	1.05	1.25	—

We find here generally better results with the mixed cultures.

4°. S. Carlsberg + Zygos. honey

CO_2 set free after days		1	2	3	4	5	7	11
(a) Glucose + pepton	f.	—	0.28	0.60	0 85	—	0 93	—
	c.	0.03	0.15	0.22	0 26	—	0.30	—
(b) Wort (maltose)	f.	0.20	0.70	0.75	0.75	—	0.80	0.80
	c.	0 22	0.45	0.70	0.77	—	0 95	1.02
(c) Saccharose + pepton	f.	0.15	0.45	—	1.05	1 25	1.25	—
	c.	0.05	0.12	—	0.27	0.42	0.70	—

The Symbiose of the bottom yeast Carlsberg with the weak honey yeast is generally favorable, especially in the culture with Saccharose and pepton.

5°. S. Carlsberg + Schizos. Pombe

CO_2 set free after days		1	2	3	4	5	7
(a) Glucose + pepton	f.	0 15	0.75	1.03	1.08	—	1.08
	c.	0.11	0.30	0.51	0.54	—	0.54
(b) Wort (maltose)	f.	0.35	0.85	0.95	1.00	—	1.00
	c.	0.35	0.77	0.97	1.00	—	1.07
(c) Saccharose + pepton	f.	0.17	0.85	—	1.25	1.25	1.25
	c.	0.08	0.47	—	0.80	0.95	1.15

In wort, the results found correspond with the results calculated; in the other liquids the fermentation is more active.

Mixed cultures of the bottom yeast Carlsberg and the races Saaz, Logos, Pombe, or honey, are cases of metabiosis, but the possibility of one symbiont producing substances having a beneficial influence upon the other smybiont must also be considered. Antagonism is usually found with mixed cultures of the races Carlsberg and Frohberg.

II

Cultures with S. cerevisiae Saaz and another race

1°. S. Saaz + S. Carlsberg

Already studied, see I 1°., Results favorable.

2°. S. Saaz + S. Frohberg

CO₂ set free after days		1	2	3	4	5	7
(a) Glucose + pepton	f.	0.05	0.20	0.46	0.75	—	1.05
	c. ·	0.02	0 05	0.11	0.25	—	0.54
(b) Wort (maltose)	f.	0.50	0 70	0 75	0.75	—	0.75
	c.	0.32	0.72	0.82	0.82	—	0.87
(c) Saccharose + pepton	f.	0.20	0.85	—	1.40	1.40	1.40
	c.	0.18	0.67	—	1.29	1.40	1.42

In wort, the results found are lower than the calculated; in Saccharose and pepton, there is no sensible difference; with glucose + pepton the fermentation is accelerated.

3°. S. Saaz + S. Logos

CO₂ set free after days		1	2	3	4	5	7
(a) Glucose + pepton	f.	0.35	0.95	1 00	1.00	—	1.00
	c.	0.20	0 47	0 47	0.50	—	0.50
(b) Wort (maltose)	f.	0.50	0.75	0 85	0.85	—	0.85
	c.	0.32	0 80	0 87	0.87	—	0.95
(c) Saccharose + pepton	f.	0.25	0.70	—	1.15	1.20	1.20
	c.	0.22	0.72	—	1.25	1.35	1.35

The results observed are better in glucose + pepton, and lower in wort and glucose + pepton.

4°. S. Saaz + Zygos. honey

CO₂ set free after days		1	2	3	4	5	7	9	11
(a) Glucose + pepton	f.	0.05	0.28	0.56	0.82	—	0.91	—	—
	c.	0.03	0.15	0.22	0.26	—	0.30	—	—
(b) Wort (maltose)	f.	0.10	0.35	0.70	0.70	—	0.80	—	0.80
	c.	0.10	0.47	0.62	0.69	—	0.90	—	1.00
(c) Saccharose + pepton	f.	0.05	0.55	—	1.25	1.40	1.40	—	—
	c.	0.06	0.25	—	0.64	0.72	0.80	—	—

The fermentation is accelerated in the case of mixed cultures, except the wort.

5°. S. Saaz + Schizos Pombe

CO₂ set free after days		1	2	3	4	5	7
(a) Glucose + pepton	f.	0.15	0.70	1.05	1.08	—	1.00
	c.	0.11	0.39	0.51	0.54	—	0.54
(b) Wort (maltose)	f.	0.20	0.90	1.00	1.05	—	1.05
	c.	0.22	0.80	0.90	0.92	—	1.02
(c) Saccharose + pepton	f.	0.15	0.85	—	1.20	1.25	1.25
	c.	0.09	0.60	—	1.17	1.25	1.25

In Saccharose + pepton, there is no sensible difference; in the other fluids the mixed cultures are more active.

The experiments with the race Saaz show a more active fermentation, when the Symbionts are the races Carlsberg, honey or Pombe. With the other races, the results are variable, however rather favorable.

III

Cultures with S. cerevisiae Frohberg and another race

1°. S. Frohberg + S. Carlsberg

Already studied, see I 2°. Symbiosis is only slightly unfavorable in wort, favorable in pepton + glucose or Saccharose.

2°. S. Frohberg + S. Saaz

Already studied, see II 2°. Favorable in glucose + pepton. Slightly unfavorable in wort and in saccharose + pepton.

3°. S. Frohberg + S. Logos

CO₂ set free after days		1	2	3	4	5	7
(a) Glucose + pepton	f.	0.40	0.92	1.00	1.00	—	1.00
	c.	0.22	0.53	0.58	0.70	—	0.92
(b) Wort (maltose)	f.	0.50	0.70	0.70	0.70	—	0.70
	c.	0.60	0.87	0.95	0.95	—	0.97
(c) Saccharose + pepton	f.	0.30	0.85	—	1.15	1.20	1.25
	c.	0.33	1.00	—	1.39	1.40	—

Only in glucose + pepton do these two topyeast races produce better results; in the other cases the results are slightly unfavorable.

4°. S. Frohberg + Zygos. honey

CO₂ set free after days		1	2	3	4	5	7
(a) Glucose + pepton	f.	0.05	0.30	0.65	0.90	—	0.90
	c.	0.06	0.20	0.33	0.46	—	0.72
(b) Wort (maltose)	f.	0.50	0.75	0.35	0.85	—	0.85
	c.	0.37	0.55	0.70	0.77	—	0.92
(c) Saccharose + pepton	f.	0.15	0.80	—	1.25	1.30	1.30
	c.	0.17	0.52	—	0.79	0.82	0.92

Favorable results with the mixed cultures; in wort the difference is slight.

5°. S. Frohberg + Schizos. Pombe

CO₂ set free after days		1	2	3	4	5	7	11
(a) Glucose + pepton	f.	0.25	0.35	1.13	1.13	—	1.13	—
	c.	0.14	0.44	0.62	0.74	—	0.96	—
(b) Wort (maltose)	f.	0.50	1.00	1.10	1.10	—	1.20	1.30
	c.	0.50	0.37	0.97	1.00	—	1.05	1.09
(c) Saccharose + pepton	f.	0.22	0.97	—	1.37	1.42	—	—
	c.	0.21	0.37	—	1.32	1.35	1.37	—

Favorable results in all the three culture liquids.

The experiments with the race Frohberg give consequently usually favorable results; only with the top race Logos is the fermentation less active.

IV

Cultures with S. cerevisiae Logos and another race

1°. S. Logos + S. Carlsberg

Already studied, see I 3°. Results favorable.

2°. S. Logos + S. Saaz

Already studied, see II 3°. Results favorable in glucose + pepton, unfavorable (slight difference) in wort (maltose) and in Saccharose + pepton.

3°. S. Logos + S. Frohberg

Already studied, see III 3°. Results only favorable in glucose + pepton.

4°. S. Logos + Zygos. honey

CO_2 set free after days		1	2	3	4	5	7
(a) Glucose + pepton	f.	0.40	1.00	1.02	1.02	—	1.02
	c	0.23	0.62	0.70	0.56	—	0.80
(b) Wort (maltose)	f.	0.60	0.85	0.95	0.95	—	1.05
	c.	0.37	0.62	0.75	0.82	—	1.00
(c) Saccharose + pepton	f.	0.30	1.05	—	1.40	1.45	1.45
	c.	0.21	0.57	—	0.74	0.77	0.85

Results favorable in all the cases.

5°. S. Logos + Schizos. Pombe

CO_2 set free after days		1	2	3	4	5	7
(a) Glucose + pepton	f.	0.43	0.98	1.03	1.03	—	1.05
	c.	0.31	0.86	0.98	1.04	—	1.04
(b) Wort (maltose)	f.	0.70	0.90	0.90	0.90	—	0.90
	c.	0.50	0.95	1.02	1.05	—	1.12
(c) Saccharose + pepton	f.	0.30	1.15	—	1.45	—	—
	c.	0.24	0.92	—	' 1.27	1.30	1.30

Results favorable in glucose + pepton, and in Saccharose + pepton, unfavorable in wort.

Mixed culture with S. Logos give favorable results in the presence of the bottomyeast Carlsberg and with the honey yeast. The results are variable with the other yeasts.

V

Cultures with Zygosaccharomyces honey and another race

1°. Zygos. honey + S. Carlsberg

Already studied, see I 4°. Results favorable in glucose + pepton and in saccharose and pepton, not favorable in wort.

2°. Zygos. honey + S. Saaz

Already studied, see II 4°. The same results as in the case of the mixed cultures with S. Carlsberg.

3°. Zygos. honey + S. Frohberg

Already studied, see III 4°. Mixed cultures give better results. There is only a slight difference in the case of wort.

4°. Zygos. honey + S. Logos
Already studied, see IV 4°.   Results favorable.

5°. Zygos. honey + Schizos. Pombc

CO₂ set free after days		1	2	3	4	5	7	11
(a) Glucose + pepton	f.	0 22	0.82	1 02	0.98	—	0 98	—
	c.	0.15	0 54	0.73	0 80	—	0.84	—
(b) Wort (maltose)	f.	0.25	0.90	1.00	1.05	—	1.10	1.20
	c.	0 27	0.62	0.77	0.87	—	1.07	1.16
(c) Saccharose + pepton	f.	0.15	0.85	—	1.25	1.25	1.30	
	c.	0.08	0.45	—	0.67	0.67	0.75	

Results everywhere favorable.

Symbiosis of honey yeast with the other yeasts employed works favorably.

VI

Cultures with Schizosaccharomyces Pombe and another race

1°. Schizos. Pombe + S. Carlsberg

Already studied, see I 5°.   Results favorable in glucose + pepton and saccharose + pepton.   There is no difference in the case of wort.

2°. Schizos. Pombe + S. Saaz

Already studied, see II 5°.   Results favorable; in saccharose + pepton the difference is very small.

3°. Schizos. Pombe + S. Frohberg

Already studied, see III 5°.   Results favorable.

4°. Schizos. Pombe + S. Logos

Already studied, see IV 5°.   A small difference, too favorable results in glucose + pepton and saccharose + pepton; unfavorable in wort.

5°. Schizos. Pombe + Zygos. honey

Already studied, see V 5°.   Results favorable.

Mixed cultures with Pombe yeast and other races, S. Logos excepted, give better results.

GENERAL SUMMARY OF THE RESULTS

A general summary of our results is contained in the following table; the favorable results are maked with +, the unfavorable with —; 0 means there is no sensible difference. The signs are placed in the following order: glucose + pepton, wort (maltose), saccharose + pepton.

	Carlsberg	Saaz	Frohberg	Logos	Honey	Pombe
Carlsberg		+ + +	+ — +	+ 0 +	+ — +	+ 0 +
Saaz	+ + +		+ — 0	+ — —	+ — +	+ + 0
Frohberg	+ — +	+ — 0		+ — —	+ 0 +	+ + +
Logos	+ 0 +	+ — —	+ — —		+ + +	0 — +
Honey	+ — +	+ — +	+ 0 +	+ + +		+ + +
Pombe	+ 0 +	+ + 0	+ + +	0 — +	+ + +	

The symbiosis under the conditions of our experiments, and with the races used is consequently generally favorable. The mixed cultures of the bottomyeasts Carlsberg and Saaz are in this respect especially interesting. The most unfavorable results are to be found in the mixed cultures of the topyeasts Frohberg and Logos. These phenomena must be considered in relation with the fact that the temperature at which our experiments were carried out (25 C.) is unfavorable for bottom yeast, but quite normal for top yeast.

With the honey yeast (Zygosaccharomyces) alone, the fermentation is slight. We found that it increased considerably by admixture of other races. The strong races, Frohberg, Logos, and Pombe, (which individually ferment with great vigor) have a mutually unfavorable influence over one another, under the conditions of symbiosis. In the case of Frohberg and Logos, there is according to Pfeffer's theory (Handbuch der Pflanzenphysiologie, Leipzic, 1897—I) much antagonism.

The culture media also have an influence; in glucose + peptone, the results are generally better than in saccharose + peptone, and in the last named medium, better than in wort with maltose.

It is difficult to classify the cases we have studied with other symbiotic phenomena. Even if we know the principal products of the fermentation, the other products that work as stimulants

or as poisons on the cells, have yet to be determined. We have not to deal with parasitism or cohabitation, or homobium, and therefore our studies cannot be classified according to Frank. (Bitrage zur Physiologie der Pflanzen—p. 123, 1876—II). We might perhaps follow the theory of Ward (Ann. Botany 1899—13-549). Behren (Handbuch Micrologie. Lafar, 1905—I 501) and Pfeffer (Handbuch 1897-I) and regard these phenomena as disjunctive or occasional symbioses; but there are here no relations to nutrition. One race does not produce really favorable or unfavorable nutrients for the other race; but rather produces certain stimulants which excite the fermentative action of the symbionts and produce favorable or unfavorable results. This is, of course, a pure hypothesis.

I prefer to give here merely the facts as I have found them, and to compare these facts (1) with those brought out by Hansen (Z. ges. Brauweisen, 1881—4,449) that mixed cultures of Saccharomyces Apiculatus and common bottom yeast give unfavorable results, and (2) the conclusions of Muller-Thurgau (Koch's Jahresbuch, 1895—6-182) that Saccharomyces Apiculatus works unfavorably on wine yeast; and lastly, I believe that my experiments confirm the general opinions held in the industry of fermentation, that mixed cultures give better results than pure yeasts.

LA DIASTASE SACCHARIFIANTE DU MALT ET LA RÉACTION DU MILIEU

Par Henri Van Laer

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L'action exercée par les ions H˙ et (O H)' sur l'activité des enzymes a été parfois comparée à celle de la température.

Dans une communication présentée l'année dernière, au IIe Congrès international de brasserie de Chicago, j'ai montré que les saccharifications effectuées par un extrait de malt suffisamment atténué sous l'action de la chaleur, sont caractérisées par l'allure décroissante du coefficient de vitesse.

Il m'a paru intéressant de rechercher, si le même phénomène ne se présentait pas avec des solutions diastasiques additionnées de quantités variables d'acide ou d'alcali.

J'ai opéré avec deux liqueurs actives, très différentes par les impuretés susceptibles de jouer le rôle de tampon entre l'enzyme et les ions H˙ ou (O H)': un extrait de malt obtenu en filtrant le produit de la macération, à froid, de 20 grammes de farine de malt et de 100 c.c. d'eau, et une solution filtrée, parfaitement limpide, de diastase en paillettes.

Cette dernière préparation provenait de la maison Chassaing et Cie de Paris; elle a été fabriquée avec un malt d'un titre d'environ 2500, l'essai étant effectué dans les conditions de la Pharmacopée française; le titre de la diastase, précipitée, de la macération froide, par trois fois son volume d'alcool à 90°, variait entre 400 et 500. Ce titre a été ramené à 100 par une ajoute de gomme.

Comme nous le verrons, l'extrait de malt et la solution de cette diastase en paillettes offrent une sensibilité très différente aux ions H˙ et (O H)'.

Les expériences ont été exécutées à la température invariable de 25° C. Le thermostat dont je me suis servi, pouvait recevoir

facilement sept ballons en verre de Iéna, contenant toujours, sauf indication contraire, 500 c.c. d'une solution d'amidon pur à 3%.

L'un des flacons servait de témoin, les autres recevaient des volumes variables (v) d'une solution acide ou alcaline $\frac{N}{10}$. Après avoir amené, par de l'eau distillée, le contenu de tous les récipients au même volume, on laissait la température des liquides s'unifier avec celle du thermostat, puis on ajoutait à chacun, un nombre identique de centimètres cubes Δ de la solution diastasique, portée au préalable à la température du bain. Le volume total (V) de chacun des systèmes d'une série était donc le même. Les valeurs de K ont été calculées au moyen de la formule des réactions unimoléculaires $K = \frac{1}{\Theta} \log. \frac{1}{1-x}$.

Rappelons que, dans cette expérience, Θ représente les temps évalués en minutes. X indique la fraction du maltose produite au bout de temps Θ. J'ai montré précédemment que la quantité totale de maltose susceptible d'être formé facilement dans une solution, contenant environ 3% d'amidon et préparée à 4 atmosphères, est égale à 90 % du poids de la matière amylacée. Pour cette raison, les valeurs de X et de K sont affectées d'un indice et représentées par les symboles X 90 % et K 90 %.

I indique la réaction à l'iode: B = bleu; V = violet; J = Jaune. Dans tous les tableaux de chiffres, reproduits dans ce mémoire, je me borne à donner les valeurs de K 90 % multipliées par 10^6; j'indique également les valeurs de X 90 % pour une prise d'essai, généralement la dernière.

SACCHARIFICATIONS EN MILIEUX ACIDIFIÉS PAR H_2SO_4 OU ALCALINISÉS PAR NaOH

Voici d'abord deux séries de résultats. La première a été obtenue avec l'extrait de malt, la seconde avec une solution de diastase en paillettes (solution à 1 %).

On constatera que dans tous les cas, l'action exercée sur le coefficient de vitesse par une concentration suffisante en ions $H^{\cdot}$ ou $(OH)'$, est la même que celle que l'on observe dans la diastase atténuée par la chaleur. Les valeurs de K, d'abord croissantes, tendent à devenir constantes pour décroître ensuite.

<div align="center">

Série I. Extrait de malt

$\Delta = 5$ c.c. $V = 520$ c.c.

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		H$_2$SO$_4$ $\frac{N}{10}$.				Na OH $\frac{N}{10}$.					
θ	Témoin		v = 1		v = 2,5		v = 7,5		v = 1		v = 2,5		v = 7,5
	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I
30	4210	B	3920	B	3706	B	2680	B	3706	B	3266	B	1203	B
60	4571	B	4571	B	3798	B	2356	B	3798	B	3446	B	1070	B
120	5982	V	5108	V	3798	V	2040	B	4155	V	3432	B	730	B
180	6315	J	5993	J	3710	J	1936	B	4137	V	3420	V	608	B
X 90 % après 180 min.	0,9270		0,9166		0,7851		0,5517		0.82		0,7577		0,2229	

<div align="center">

Série II. Diastase en paillettes; (solution à 1 %)

$\Delta = 10$ c.c. $V = 520$ c.c.

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		H$_2$SO$_4$ $\frac{N}{10}$.				Na OH $\frac{N}{10}$.					
θ	Témoin		v = 1		v = 2,5		v = 7,5		v = 1		v = 2,5		v = 7,5
	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I
30	3273	B	2680	B	1770	B	1220	B	3273	B	3140	B	2980	B
60	3548	B	2295	B	1043	B	801	B	3340	B	3153	B	2711	B
120	3805	V	1879	B	577	B	422	B	3682	V	3395	V	2025	B
180	4230	V	1626	B	465	B	309	B	3710	V	3420	V	1962	B
X 90 % après 180 min.	0,8307		0,4904		0,1754		0,1202		0,7851		0,7577		0,5566	

Les extraits des divers malts avec lesquels j'ai opéré, ont toujours donné, pour K, des valeurs dont les variations présentaient l'allure de celles reproduites dans la série I. Une préparation de diastase en poudre de Kahlbaum se comportait de la même facon.

Le produit en paillettes de Chassaing ainsi que d'autres simi-
laires ont fourni constamment, pour K, des valeurs offrant les
particularités qui ressortent de l'examen des chiffres de la série II.

On remarquera que pour des quantités équivalentes d'acide
sulfurique et de soude *mises en oeuvre*, la diastase de l'extrait de
malt paraît moins sensible à l'ion $H^{.}$ qu'à l'ion (OH)'; l'inverse
s'observe pour la diastase en paillettes. C'est que les impuretés
qui accompagnent l'enzyme ne sont pas les mêmes dans les deux
solutions; dans l'extrait du malt, elles agissent surtout comme
tampon entre la diastase et l'acide, tandis que dans la solution
de diastase en paillettes, c'est entre l'enzyme et l'alcali.

Toutes les liqueurs précédentes, à l'exception de celle pour
laquelle v = 7.5 c.c. de NaOH $\frac{N}{10}$, étaient acides à la phénolphta-
léine; tous les milieux contenant H_2SO_4 étaient, au départ, très
légèrement alcalins ou neutres au méthylorange, mais après 180
minutes, la réaction, à cet indicateur, était devenue franchement
acide; les solutions additionnées de soude accusaient aussi, à
la fin de la réaction, une légère décroissance de l'alcalinité à
l'hélianthine; cette diminution atteignait 1 à 3 c.c. de $H_2SO_4 \frac{N}{100}$,
pour 100 c.c. du liquide saccharifié.

Une variation dans le même sens, s'élevant parfois à 6 c.c. de
Na OH $\frac{N}{100}$, se constate pour l'acidité à la phénolphtaléine.

Ces légères diminutions de l'acidité à la phénolphtaléine et de
l'alcalinité au méthylorange affectent aussi les milieux ne con-
tenant que l'amidon et la solution diastasique, sans aucune
ajoute d'acide ou d'alcali. Elles résultent probablement de
phénomènes secondaires de protéolyse avec formation de ma-
tières azotées amphotères.

Les Phosphates Primaires et Secondaires et les Impuretés de la Préparation Diastasique

On a préparé, avec Na H_2 PO_4, et KH_2 PO_4, des solutions dont
l'acidité à la phénolphtaléine était égale à celle d'une solution de
H_2 $SO_4 \frac{N}{10}$; de même du Na_2HPO_4 et du K_2HPO_4, ont servi à la
préparation de liqueurs dont l'alcalinité au méthylorange était la
même que celle d'une solution de NaOH $\frac{N}{10}$.

Des séries parallèles de saccharifications ont alors été opérées. Elles ont donné les résultats suivants. Les chiffres obtenus avec Na H$_2$ PO$_4$ étaient identiques à ceux qu' à donné KH$_2$ PO$_4$, et ceux fournis par Na$_2$ HPO$_4$ les mêmes que ceux des saccharifications avec K$_2$HPO$_4$.

Tous ces sels, chimiquement purs, provenaient de chez Kahlbaum.

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Série III. Extrait de malt

$V = 510$ c.c.; $\Delta = 5$ c.c.; $v = 5$ c.c.

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θ	Témoin		H$_2$SO$_4$		Na OH		Na H$_2$ PO$_4$		Na$_2$ HPO$_4$	
	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I
30	3833	B	3618	B	3586	B	4380	B	3780	B
60	4096	B	3693	B	——	B	4725	B	3618	B
120	4547	V	3984	V	3445	V	5809	V	3986	V
180	5520	J	4651	V	3489	V	6243	J	4676	V
$\overline{X}$ 90 % après 180mn	0,8985		0,8545		0,7645		0,9248		0,8560	

On note ici l'action accélératrice bien connue des phosphates primaires et l'action retardatrice des phosphates secondaires.

Cependant l'accélération produite par les phosphates primaires ne se manifeste plus avec la diastase en paillettes, comme on peut le voir dans la série IV.

SÉRIE IV. Solution à 2 % de diastase en paillettes

V = 520 c.c.; Δ = 5 c.c.; v = 5 c.c.

θ	Témoin		KH$_2$PO$_4$		K$_2$HPO$_4$	
	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I
30	4063	B	3970	B	3526	B
60	4033	B	3530	B	3193	B
120	4071	V	3331	B	3135	B
180	4083	V	3005	V	3927	V
X 90 % après 180 minutes	0,8159		0,7122		0,7028	

Ici, le phosphate primaire, tout en étant moins nocif que le phosphate secondaire, n'en ralentit pas moins la vitesse de saccharification de l'amidon.   Des expériences identiques, exécutées avec des doses des phosphates plus faibles ou plus fortes, ont fourni des résultats ayant la même signification.

ACTION DES BASES FAIBLES

Comparons le ralentissement de l'action diastasique produit par une base forte, la soude par exemple, avec celui auquel donnent lieu les bases faibles dans les mêmes conditions.

J'ai choisi comme représentants de ces dernières l'ammoniaque et la triéthylamine.

Les séries suivantes de résultats montrent les variations de la vitesse réactionnelle de saccharifications opérées en présence de quantités équivalentes de ces deux bases et de soude.

SÉRIE V. Extrait de malt

$V = 520$ c.c.; $\Delta = 5$ c.c.; $v = 7.5$ c.c. de solution alcaline $\frac{N}{10}$.

θ	Témoin		Na OH		[N(C₂H₅)₃H] OH		(NH₄) OH	
	K 90 % 10⁶	I	K 90 % 10⁶	I	K 90 % 10⁶	I	K 90 % 10⁶	I
30	7226	B	2080	B	2056	B	2923	B
60	8143	V	1726	B	1738	B	2646	B
120	10412	J	1495	B	1516	B	2602	B
180			1435	B	1393	B	2632	V
X 90 % après 180min	0,9437		0,3383		0,3422		0,5128	

SÉRIE VI. Diastase en paillettes en solution à 2%

$V = 520$ c.c.; $\Delta = 5$ c.c.; $v = 7.5$ c.c. de solution alcaline $\frac{N}{10}$.

θ	Témoin		Na OH		[N(C₂H₅)₃H] OH		(NH₄) OH	
	K 90 % 10⁶	I	K 90 % 10⁶	I	K 90 % 10⁶	I	K 90 % 10⁶	I
30	4760	B	1143	B	1193	B	1960	B
60	5618	B	926	B	948	B	1831	B
	9593	J	764	B	814	B	1947	B
180			690	B	713	B	2172	V
X 90 % après 180min	0,9294		0,1902		0,2013		0,4161	

La nocivité des bases augmente avec leur force sans cependant être en rapport avec celle-ci. Rappelons que si l'on représente par 100 la force de l'hydrate de lithium, celle de l'hydrate de sodium est égale à 99, celle de l'hydrate de triéthylammonium à 14, celle de l'hydrate d'ammonium à 2. Or, la nocivité de la triéthylamine n'est que très peu inférieure à celle de la soude, et celle de l'ammoniaque est élevée, quand on tient compte de la force de cette base. Cela provient de ce que les impuretés

agissant comme tampon entre les ions (OH)' et l'enzyme, immobilisent, dès le commencement de la réaction, une quantité plus importante de soude que de triéthylamine ou d'ammoniaque.

La base forte paraît ainsi moins nocive qu'elle ne l'est en réalité. Si les solutions en contenaient aucune substance capable de modifier l'équilibre entre l'hydrate et ses ions, le degré de nocivité des bases serait exactement en rapport avec le nombre d'ions (OH)' qu'elles cèdent à chaque unité de volume de la solution.

Action de Différents Acides

L'examen de la vitesse de la saccharification de l'amidon, en présence de quantités équivalentes de différents acides, montre que les valeurs obtenues pour K ont une tendance bien nette à classer les acides dans le même ordre que celui que détermine leur force.

On remarque cependant une influence bien nette des anions.

Ainsi, dans toutes mes expériences, j'ai observé que l'acide sulfurique s'est toujours montré plus nocif que l'acide chlorhydrique, et l'acide phosphorique moins nocif que l'acide tartrique, alors que, si l'on envisage la force respective de ces agents, l'acide chlorhydrique devrait être plus actif que l'acide sulfurique, et que l'acide phosphorique devrait l'être plus que l'acide tartrique.

L'anomalie relative aux acides Chlorhydrique et sulfurique s'observe d'ailleurs dans les courbes tracées en 1878 par Kyeldahl[1]: elles ont pour " ordonnés les accroissements du sucre et pour abcisses des centimètres cubes d'acide normal au 1/10."

Les branches descendantes de ces courbes établissent que l'acide sulfurique est le plus déprimant et l'acide acétique le moins.

L'acide chlorhydrique se range, sous ce rapport, après l'acide sulfurique.

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[1] *Medd. fra Carlsberg Laboratoriet* 1878 page 173 (texte danois) et p. 149 (texte français).

SÉRIE VII. Diastase en paillettes en solution à 2%:

$V = 517.5$ c.c.; $\Delta = 5$ c.c.; $v = 7.5$ c.c. de solution acide $\frac{N}{10}$.—

θ	Témoin		H₂SO₄		HCl		Ac. Oxalique		Ac. Tartrique		Ac. Phosphorique		Ac. Acétique	
	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I
30	5776	B	1026	B	1140	B	1720	B	1733	B	1903	B	3566	B
60	5793	B	568	B	608	B	936	B	1075	B	1128	B	3046	B
120	5874	V	304	B	329	B	509	B	655	B	681	B	2137	B
180	6302	J	216	B	232	B	395	B	498	B	546	B	1867	B
X 90% après 180min.	0,9266		0,0855		0,0916		0,1509		0,1867		0.2027		0.5387	

SÉRIE VIII. Extrait de malt

$V = 517.5$ cc.; $\Delta = 5$ c.c.; $v = 7.5$ c.c. de solution acide $\frac{N}{10}$.—

θ	Témoin		H₂SO₄		HCl		Ac. Oxalique		Ac. Tartrique		Ac. Phosphorique		Ac. Acétique	
	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I	K 90% 10⁶	I
30	6013	B	4726	B	5600	B	6530	B	7773	B	9386	B	9386	B
60	7100	V	4333	B	5905	B			6861	V	11525	V	11525	V
120	9380	J	4078	V	6420	V	6420	V	6799	J	9380	J	9380	J
180			4013	J	6351	J	6351	J	6351	J				
X 90% après 180min.	0,9251		0,6759		0,8303		0,8303		0,8472		0,9251		0,9251	

Les acides sulfurique et chlorhydrique gênent la saccharification; les autres la stimulent, du moins au début. Au moment où l'expérience a été interrompue, toutes les solutions, à l'exception du témoin et de celle qui avait été acidifiée par l'acide acétique, présentaient une réaction franchement acide au méthylorange. Cette dernière était neutre à cet indicateur. On voit que des doses équivalentes de différents acides se comportent d'une

façon très différente, suivant la préparation diastasique mise en oeuvre, et qu'aux doses où les acides forts sont gênants, des quantités équivalentes d'acides faibles peuvent stimuler l'action de la diastase.

Mode d'Action des Ions $H^{\cdot}$ et $(OH)'$ sur l'Enzyme

Demandons-nous si l'atténuation de l'activité diastasique par les acides et les alcalis, résulte d'une destruction partielle de l'enzyme, ou du passage de celle-ci à l'état d'une combinaison inactive, dont elle pourrait être retirée intacte après neutralisation de l'acide ou de alcali.   Ces deux éventualités se présentent; cette atténuation d'activité dépend essentiellement de la quantité d'acide ou d'alcali mise en présence de la diastase.   Si l'acidité ou l'alcalinité de la solution active correspond à celle d'une liqueur $\frac{N}{20}$, la diastase est complètement détruite; si l'acidité ou l'alcalinité est dix fois + faible ($\frac{N}{200}$), il n'y a que destruction partielle.   Cela se voit très bien par les chiffres fournis par l'expérience suivante:

Série IX.   Deux portions de solution diastasique (diastase en paillettes, en solution à 2 % et extrait de malt) égales à 10 c.c. ont été additionnées de 10 c.c. de NaOH $\frac{N}{100}$.   On a laissé en repos pendant 12 heures, puis on a neutralisé la liqueur acide par ajoute de 10 c.c. de NaOH $\frac{N}{100}$, et la liqueur alcaline par ajoute de 10 c.c. de $H_2 SO_4 \frac{N}{100}$.   Une troisième portion de solution diastasique de 10 c.c. a reçu, à ce moment, 20 c.c. de la solution de sulfate de soude obtenue en ajoutant, à 10 c.c. de $H_2SO_4 \frac{N}{100}$, 10 c.c. de NaOH $\frac{N}{100}$.

Les essais de saccharification ont été exécutés dans les conditions habituelles avec 20 c.c. de chacune de ces solutions. (V = 520).

	Diastase en paillettes					Extrait de Malt				
θ	Témoin		Diastase ayant été au contact des ions H·.—		Diastase ayant été au contact des ions (OH)'.		Témoin		Diastase ayant été au contact des ions H· —		Diastase ayant été au contact des ions (OH)'.—
	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I	K 90 % 10^6	I
30	15666	V	7236	B	10120	B	9040	B	7886	B	8090	B
60	19433	J	5886	B	12010	V	11208	V	7176	V	11208	V
120			4171	V	9435	J			5604	V	9472	J
X̄ 90 % au bout de 60 minutes	0,9313		0,5886		0,8097		0,7874		0,6284		0,7874	

Malgré un séjour prolongé au sein d'une solution ayant une acidité ou une alcalinité correspondant à celle d'une liqueur $\frac{N}{200}$, la diastase n'a été que partiellement détruite. Elle a retrouvé une activité importante après neutralisation.

Or, dans toutes les expériences précédentes, la plus forte acidité ou la plus forte alcalinité réalisée, en supposant même que les impuretés n'aient pas agi comme " tampon," n'a jamais dépassé celle d'une liqueur $\frac{N}{500}$, et la durée de contact a été au plus de trois heures. Nous pouvons donc dire que dans ces liqueurs, l'inhibition résultait uniquement de la formation d'une combinaison inactive, contractée entre l'enzyme et l'acide ou l'alcali. Par conséquent, la perte d'activité constatée au cours d'une saccharification opérée en présence d'un excès d'ions H· ou (OH)', est la résultante de trois effets principaux:

1° accroissement d'activité due à la disparition d'un certain nombre d'ions H· ou (OH)', sous l'influence des substances agissant comme " tampon "; 2° destruction irréversible d'une portion de la diastase; 3° immobilisation temporaire d'une partie de l'enzyme.

La molécule d'amylase paraît avoir un caractère amphotère, ses propriétés spécifiques dépendant à la fois des groupes basiques et acides qu'elle contient.

FURTHER RESEARCH ON THE PROTEOLYTIC ENZYM OF MALT

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The investigation here described is concerned mainly with the proteolytic strength of barley malt as influenced by the presence of lactic acid.

In the main it was found that:

I. The study of the proteolytic activity of malt is *facilitated* by the presence of lactic acid, propagated through bacterial activity in the mash.

II. Through the influence of this bacterial acidity, the proteolytic activity of malt is found to be *increased* to an extraordinary degree. This was in every case established by means of the gelatine test, and also by auto digestion. (See below.)

III. The proteolytic activity of malt extracts prepared by mashing malt with water without the addition of lactic acid is quite low, compared with that of extracts prepared by mashing the malt with acidulated water under the same conditions.

VI. Through the influence of this bacterial acidity, complete digestion of the coagulable albumen contained in the malt extract was affected, whereas Fernbach and Hubert succeeded in proteolysing not more than 45%.

V. *The peptic enzym contained in the malt is evidently locked up (combined with some base, presumably of albumenous nature), and becomes active through liberation by bacterial acidity.*

VI. The proteolytic activity of malt extracts, prepared by mashing the malt with water, acidulated by the addition of bacterial lactic acid, exerts itself at relatively low temperatures (5°-30° C.) and is quite effective in splitting albumen at *such low* temperatures; it reaches its optimum at a temperature of approximately 30° C., and is weakened at temperatures above 30° C., being destroyed rapidly at a temperature approximating 50° Centigrade.

At temperatures below 30° C. its activity gradually decreases, but at 10° C. it is still quite active, then *rapidly* decreases until 0° C. is reached, where it is practically nil.

These findings are contrary to opinions, based upon the results of investigations heretofore made, according to which the optimum temperature of peptic activity was given as from 40°-50° C., and the destructive temperature at about 65° C., by Wahl and Nilson, which findings were corroborated by Weiss, Ehrich and Hantkte. (See literature below.)

VII.   Substituting mineral or commercial acid for bacterial acid does not result in increasing the peptic activity of the malt extract.

This finding suggests a difference in the physical state of the bacterial lactic acid, due possibly to dissociation (ionization). Investigations of this are to form the basis for research work now in progress, a number of conductivity measurements having already been made.

VIII.   The addition of a small quantity of bacterial lactic acid to a brewer's mash increases the yields obtained from the malt through an increase in peptic activity.

IX.   Commercial malts, as found on the market, vary greatly as to the peptic strength of the extracts produced therefrom under identical conditions.   High kiln-dried malts develop a lower peptic strength than low kiln-dried malts; malts of the Manchuria type develop higher peptic strength than malts of the Bay Brewing type.

The scope of the work, from the results of which the above conclusions were reached, included the investigation of:

I   The influence of different degrees of acidity on the peptic activity of malt extracts prepared, (a) at different temperatures, (b) with different periods of maceration, and (c) with different degrees of fineness of grist.

II.   The effects of time and temperature on the peptic activity as determined, (a) by auto-digestion, (b) by the liquefying effect on gelatine.

III.   The substitution of the bacterial acid by various other acids, mineral and organic.

IV. The peptic strength of various commercial malts prepared from (a) low and high kiln-dried malts, (b) malts prepared from different types of barley.

HISTORICAL

The existence of a proteolytic enzym in germinating barley was unknown until 1847, when Gorup-Besancz made the first experiments to demonstrate its presence. These results were published in the Berichte[1] and later confirmed by the work of Neumeister.[2]

Gorup found that a solution of the enzym obtained from kilned malt, when allowed to act on blood fibrin yielded soluble products which gave reactions usually considered typical of peptic digestion. Neumeister, working with a solution of enzym derived from green malt repeated these experiments and obtained results which were in excellent agreement with those of Gorup.

In 1893 R. Wahl,[3] in a paper read before the United States Brewmasters' Association, for the first time drew attention to the importance of the albuminoids in beer. He pointed out that similar to the manner in which starch is dissolved during the mashing process, and by means of diastase converted into dextrine, iso-maltose and maltose, so the insoluble albuminoids of barley, partially during malting but more extensively during mashing, are by means of peptase converted into three different forms of albuminoids—proteins, peptones, and amides, the process of peptonization progressing as long as the mash is held at a temperature favorable to the operation of the peptic enzym. He further showed that the first named of these products of peptic digestion may be compared to soluble starch: They cause turbidities in beer; the peptones may be compared to dextrine: They remain in the beer, and like dextrine, give it fuller body and increase the headiness, that is, the capacity of holding foam; the amides are the digestible albuminoids: Similar to sugar, they

[1]Berichte der Deutschen Chem. Ges. 1847, **7**, 1478, 1875, **8**, 1510, 1876, **9**, 673.

[2]Amer. Brewers' Rev. **7**, 185, 201.

[3]Amer. Brewers' Rev., **7**, 185, 201.

serve as a food for the yeast, and, like sugar, they are removed from the beer and stored up in the yeast.

The following year Wahl[1] in collaboration with Nilson, published the results of elaborate researches regarding the nature and importance of the albuminoids in beer, which confirmed the views of Wahl as expressed by him in 1893. Judging from the amount of proteins contained in malt extracts, prepared at various temperatures, the optimum temperature for the activity of the peptase they found to be 45° Centigrade, and that this activity was maintained for all temperatures within the range of 38°-57° C. above 57° C. there was a rapid decrease until 65° C. was reached, at which temperature the peptic activity was no longer demonstrable. From these experiments it was further concluded that by keeping the doughing-in temperature down to about 38° C. the amount of useful albuminous substances— peptones and amides (which are dissolved during the process of mashing)—will be increased, and less of the injurious albuminous substances will be found in the finished beer than where high temperatures are employed in doughing-in.

In 1895 these results obtained by Wahl and Nilson were corroborated by Erich[2] and also by Hantke.[3]

Windisch and Schellhorn in 1900[4] made a series of experiments which demonstrated the presence of proteolytic enzym in malt, by:

1. The liquefaction of gelatine.
2. Auto-digestion of aqueous extracts.
3. The preparation of an active proteolytic substance by extraction with glycerol.

About this time Fernbach and Hubert,[5] and Petit and Labourasse,[6] both parties working independently, came to practically the same conclusions.

[1]Amer Brewers' Rev., **7**, 580.

[2]Der Bierbrauer, 1895, 162.

[3]Brewer and Maltster, 1895, 1146.

[4]Wochenschr. Brauerei, 1900, 17, 334-6, 400-13, 437-9, 449-52.

[5]Comptes Rend. de l'Acad. des Sciences, 1900, 131, 293-5.

[6]Comptes Rend. de l'Acad. des Sciences, July, 1900.

Fernbach and Hubert demonstrated the existence of a proteolytic enzym in malt by auto-digestion of the coagulable albumin in cold water infusions of malt at a temperature up to 70° C. In this way as much as 45% of the original coagulable albumin was transformed. These authors also manifested that the enzym was not destroyed by kilning.

F. Weiss[1] the same year confirmed the discovery of the proteolytic enzym in germinating barley, and made the additional discoveries that the action of the malt enzym is greater under similar conditions than that of pepsin, and that the temperature of mashing which is most favorable to the extraction and peptonization of the albumenoids is 50° C.

Lintner, in 1902,[2] succeeded in separating the enzym by concentrating the malt extract through the freezing out of the water.

In 1903 Weiss[3] published the results of additional experiments, from which he concluded that two enzyms must be present in malt, a peptase and a tryptase. The peptic action proceeds rapidly at 52° C. and quickly attains its final stage, whereas the tryptic action is slow, the most favorable temperature ranging from 35° to 48° C. and continues until all peptic products have been decomposed.

Nilson, in 1903,[4] and again in 1904,[5] showed that the peptonizing of the albuminoids by peptase was conditioned to some extent on the acidity of the mash. He found that with the increase of the percentage of the lactic acid in the mash the albuminoids found in the wort also increased considerably. He further expressed the view that the germ and endosperm of the barley do not contain *free* enzyms in sufficient quantity to make germination possible, and that the enzyms are set free by chemical action of the acids produced by the living bacteria of the barley corn, which bacteria, in exchange for the soluble carbohydrates and albuminoids extracted by the steeping water from the barley,

[1]Z. Physiol. Chemie, 1900, 31, 79.

[2]Z. Ges. Brauw. 25, 365-8.

[3]Comptes Rend des Trav. des Labor de Carlsberg, 5, 135-285.

[4]Amer. Brew. Rev. 17, November. 18, 294-7.

[5]Amer. Brew. Rev. 18, 294-7

send back into the germ and endosperm the lactic acid which dissolves the insoluble albumen, and thereby sets free the enzyms.

During the same year P. Schidrowitz[1] published a paper in which he described a method for the approximate determination of the proteolytic capacity of malt dependent upon gelatine liquefaction. The results, although in every way satisfactory and comparable among themselves, were followed in 1904[2] by further experiments intended to make the method of practical value by basing it on the use of standard materials.

Weiss later found[3] that the proteolytic enzyms of malt will attack albumin of any origin, animal or vegetable, so that the albumoses of wort (malt extract) can be increased if desired by the addition of foreign albumins. The peptase was found to withstand the operation of precipitation by alcohol, but not the tryptase.

In connection with these experiments Weiss investigated the influence of acidity on the extraction of the nitrogenous substances, obtaining results which were in good agreement with those of Nilson.[4]

Weiss also made a series of experiments with malt extract containing the proteolytic enzym and using wheat glutin as a substrate,[5] found the law of Schuetz to be valid, namely that the amount of protein digested by a given amount of proteolytic enzym is proportional to the square root of the time required for digestion.

H. Schjerning, in a paper published in 1906,[6] stated the results of his investigations on the formation and transformation of the protein constituents of barley, during growth, ripening, and storage, and obtained much valuable information therefrom. In 1910[7] he made public further experiments on the transformation of the proteins in barley during malting, carried out on malts

[1]J. Federated Inst. Brg. **9,** 361-82.
[2]J. Federated Inst. Brg. **10,** 166-72.
[3]Z. ges. Brauw. **27,** 385-9, 405-7, 420-3, 440-5.
[4]Amer. Brewers' Rev., **17,** November.
[5]Meddeleser frs. Carlsberg Lab. **5,** 1903, 127.
[6]Compt. Rend. Trav. Labor. Carlsberg, 1906, **6,** 229-307.
[7]Compt. Rend. Trav. Labor. Carlsberg, 1910, 8, 169-395.

grown and kiln dried in the laboratory, which proved equally instructive. As a result of these experiments he concluded that the insoluble proteins of barley are entirely transformed in the malting process and changed into water soluble substances through the influence of proteolytic enzymes.

H. T. Brown who in a series of experiments has studied the migration of nitrogen from the endosperm to the embryo during the malting process[1] estimates that about 35-40% of the nitrogen reserves of the endosperm pass into the young plant, so that a very considerable proportion of this nitrogen must have been converted from the form of insoluble protein into soluble and diffusible compounds before the migration could take place. He also made experiments on the nitrogen constituents of malt which are soluble in cold water and not precipitated by boiling[2] which were present in the finished malt, and was able to determine about 66% of the total.

PROPOSITION AND METHODS

Before proceeding to give in detail the results of my various investigations, it will be necessary for a proper understanding of the same, to state, at the outset, the methods of work employed and to define a number of terms which will be employed in the statement of the results which follows.

The *bacterial lactic acid* liquor, referred to in this paper as bacterial acid, or bacterial lactic acid, and which was employed in the acidulation of the water used in the malt extractions to the required degree of strength, was prepared in the following manner:

A mixture of preferably about one part of crushed malt and four parts of water, inoculated with lactic acid ferment, was subjected to a temperature varying between 50° and 60° C. maintained for about 30 minutes to destroy all organisms except the one to be propagated for producing the desired acid, and holding the temperature of the mash at 50° to 55° C. for about 24 to 48 hours, during which time from 1 to 2% of lactic acid is formed.

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[1]Trans Guiness Research Lab., 1906, I, Pt. 2, 284-7.

[2]J. Federated Inst. Brg , 1907, 13, 394-446

The grains are then separated from the liquid, and same is used for the malt extractions made as follows:

One part, either of finely ground malt (Seck mill set at 1.0) or of coarsely ground or crushed malt (Seck mill set at .5), is extracted with four parts of the bacterial liquor above mentioned, previously diluted with water so as to give the desired strength of acidity. Varying temperatures were used for the extractions as specified below.

The peptic strength of the malt extracts was determined by auto-digestion and by means of a modified " gelatine liquefying strength " method of Schidrowitz. In every instance the peptic strength of the malt extract was compared with that of a standard solution of pepsin of known strength. The method of conducting the test, as well as the preparation of the pepsin standard, are given below.

Preparation of the Gelatine. 32 grams of gelatine are dissolved in 318 cc of distilled water by gently heating the same. $\frac{1}{3}$ of a gram of finely ground egg albumen dissolved in 50 cc of distilled water, is then added and the gelatine solution cooled to 52° C. The temperature is then raised to 85° C. in 5 minutes, and then to 100° C. where it is held for 10 minutes. While still hot the gelatine is filtered into a glass beaker containing 0.5 gram of thymol, which readily dissolves in the liquefied gelatine. The solution is then tubed, each tube receiving 6 cc, and the tubes closed with cork stoppers to prevent evaporation.

Method of work. (*Testing of proteolytic strength.*) The gelatine tube is gently warmed, preferably in a thermostat or water bath, until the contents are liquefied. 5 cc of the liquid under examination are then added to the tube. A blank is prepared at the same time containing 5 cc distilled water. The tubes are then placed in an incubator held at 37.5° C. and incubated for 4 hours. After this they are placed in ice water at 2° C. and the time required for solidification of gelatine is noted. From the number of minutes required by the tube containing the liquid under examination, the time required for the solidification of the blank is subtracted, and the results tabulated for purposes of comparison. It must be remembered that a malt extract in which the enzym has been

destroyed, and which contains from 1% to 2% of lactic acid, has a slight power to liquefy gelatine, to the extent of requiring from 1 to 2 minutes longer to solidify than the blank.

Pepsin Standard. 0.15 grams of pepsin of 10,000 strength are mixed with 10 grams of powdered sugar, and dissolved in 100 grams of distilled water. 5 cc of this solution are added to a gelatine tube. The contents of a tube so prepared requires 7 minutes for solidification.

The amount of *coagulable albumen* remaining in the malt extracts after the same had been subject to the action of the peptonizing enzym for a given period and at a given temperature, was determined by means of the *coagulation test* conducted in the following manner:

The extract was filtered perfectly clear and then heated to 75° C, where it was held for 30 minutes and then allowed to cool to 25° C. 10 cc of this solution were introduced into a centrifuge tube graduated in $\frac{1}{10}$ cc. The tube was placed in the centrifuge and run for a period of 4 minutes. at a speed of about 2500 revolutions per minute. The amount of coagulable albumen in the tube is then read in terms of $\frac{1}{10}$ of cc.

Corrections: In all of the results, as stated, corrections have been made for the amount of extract of varying quality introduced into the mash through the acidulation by means of the bacterial lactic liquor, by subtracting both from the values obtained for the extract and albumen, for instance, the amount of extract and also the amount of albumen introduced into the mash, as a result of the method of acidulation employed.

THE DETAIL

Having stated the essential points necessary to an understanding of the following, I will now proceed to give in greater detail the methods of work according to which the separate questions which present themselves, were attacked.

I. 1. *To what extent does the peptic activity of malt extract increase through the presence of lactic acid?*

In order to determine this, extractions of malt, finely ground and coarsely ground, each constituting a separate set, were

made with water acidulated to varying degrees of strength with bacterial lactic acid:

(a) *Water not acidulated.*

Results: In this set the proteolytic strength was found to be very low, giving a gelatine test of 2 minutes; this remained constant for temperatures up to 50° C. The coagulable albumen was very high. (0.20%)

(b) *Water acidulated to bring the amount of acid up to 0.01, 0.02, 0.03, 0.04, 0.05%.*

Results: These low acidities effected a slight increase only, in the peptic strength, which was directly proportional to the degree of acidulation. The gelatine test gave 3-6 minutes values. The coagulable albumen slightly decreased, amounting to 0.18% except at temperatures above 50° C.

(c) *Water acidulated to bring the amount of acid up to 0.1%, 0.2%, 0.3%, 0.5%.*

Results: A marked increase in the peptic strength was manifested. The gelatine test now required from 7-12 minutes, except at the higher temperatures (50° C.). The coaguable albumen had decreased to about .015%.

(d) *Water acidulated to bring the amount of acid up to 1.0%, 1½%, and 2%.*

Results: In this set the gelatine test was found to vary directly with the per cent. of acidity, the time required for the gelatine to solidify being 14-25 minutes. This was not influenced by changes in temperature except above 50° C. The coagulable albumen exhibited only a slight change, the higher acidulations giving better (lower) value. (0.12-0.14%).

2. *What is the influence of the temperature on the peptic activity of malt extracts rendered acid by varying amounts of lactic acids?*

Extractions of malt finely ground and coarsely ground, were made with water acidulated to the various degrees above specified, with bacterial lactic acid, at temperatures of 0°, 3°, 10°, 20-22°, 30-32°, 40-42° and 50-52° C.

Results: At 0° C.-3° C. the peptic activity is very low and increases gradually up to 10° C. more rapidly from 10-22° C. and reaches its optimum at 25°-30° C. Above 30° C. it decreases

with increase of temperature.   Around 52° C. (50-55° C.) the malt extract loses all enzymatic strength, that is, it is rapidly destroyed, (in a few minutes).

3. *What is the influence of the time of maceration on the peptic activity of malt extracts rendered acid by various amounts of bacterial lactic acid.*

Bacterial acid of varying strength was taken for the extraction of finely ground and coarsely ground malt at different temperatures and different periods of maceration.   The time of maceration in each case was 15 minutes, 30 minutes, 60 minutes, 90 minutes and 3 hours, respectively.

Results: The peptic strength remained practically constant in the case of macerations of 15 and 30 minutes' duration.   From 30 minutes to 1½ hours a slight increase in peptic strength was observed; while from 1½ hours to 3 hours there was no apparent difference.   When higher temperatures (30° C.-50° C.) are maintained, the longer periods of extraction (1-3 hours) show a decrease in peptic strength as compared with the shorter periods of extraction.   (15 minutes-1hour.)

4. *Complete Mashes.*

Besides these series of experiments, complete mashes were made as follows: Finely ground malt was mashed with 4 parts of water plus an amount of bacterial lactic acid to bring the acidity to the required strength.   The mashes were made with water and the various degrees of acidulation above specified. The malt was macerated at 15° C. for 1 hour, raised to 67.5° C. in 20 minutes, and kept at this temperature for 30 minutes, to effect the inversion of the starch by the diastase of the malt, and then raised in 15 minutes to 75° C, kept at 75° C. for 15 minutes until complete inversion took place.

Results: A material increase in the percentage of extract was observed with an increase in the percentage of acidulation, which increase was directly proportional to the per cent. of lactic acid present in the mash water.   For instance, the plain water mash had an extract of 15.46% and an albumen of 1.14%; water acidulated to an extent of 0.01%, extract 15.76%; albumen 1.20%; acidulation 0.05%, extract 15.75, albumen 1.28%; acidulation 0.1%, extract 16.21%, albumen 1.50%.

From 0.6-0.9% of acidulation there was no increase in the per cent. of extract and only a slight increase in the per cent. of albumen. From 0.9-2.0% there appears to be a decrease in the per cent. of extract (after corrections had been made for the substances introduced through the method of acidulation employed). This decrease amounted to 3% in the case of the mash acidulated to the extent of 2%. There was no material increase in the percentage of sugar after corrections were made.

Acidity of the Mash. The percentage of lactic acid present in the non-acidulated water mash amounted to 0.038%. The percentage of lactic acid in the acidified mashes increased only in amount corresponding to the per cent. of acidulation until 0.07% of acidulation had been reached. From this point there occurred an apparent loss in the acidity after corrections for the amount of acid added had been made. With acidulations from 0.5-2% the apparent loss amounted to from 0.06-0.15%.

II. *A. The effects of time and temperature on peptic activity, as determined by auto-digestion.*

Results: Water-extract, coagulable albumen, average of 10 tests   = 0.20%

(a) Extracts of malt prepared with various degrees of acidulation, 1.0%, 1.5% and 2% respectively, and held at 0° C. for 3 days showed no decrease in coagulable albumen, which   = .14%

(b) Extracts prepared as above and held at 3° C. show no decrease in coagulable albumen which remains = .14%

(c) Held at 9° C. for 24 hours such extracts showed a marked decrease in coagulable albumen which is reduced to approximately   = .11%

(d) Held at 20° C. (room temperature) for 6 hours no apparent change in the coagulable albumen occurs
                                                                     = .11%

(e) Held at 30° C. for 4 hours the amount of coagulable albumen shows a very marked decrease, being
                                                                     = 0.08%

(f) Held at 40° C. for 1 hour the amount of the coagulable albumen again increases, indicating that this temperature is less favorable to the activity of the enzym

than the temperature of 30° C. Coagulable albumen
= 0.12%

(g) Held at 50° C. for 1 hour the amount of coagulable
albumen continues to increase, indicating the gradual
destruction of the enzym. Amount of coagulable
albumen   = 0.125%

(h) Held at 60° C. for 15 minutes the amount of coagulable
albumen reverts to approximately the original value,
indicating that the enzym has been destroyed.
Coagulable albumen   = 0.145%

(i) Holding at 70° C. the same result as above is obtained
at the end of 3 minutes. Coagulable albumen
= 0.145%

*II. B. The effects of time and temperature on peptic activity, as
determined by the power of liquefying gelatine.*

Results: (a) Extracts of malt prepared with various degrees of
acidulation from 0.5-1%, 1.5% and 2% respectively, and held
at 0° C. for 3 days, showed no decrease in peptic strength.

(b) Extracts prepared as above and held at 3° C. show but a
slight decrease in peptic strength corresponding to a 2-4 minute
decrease in gelatine test.

(c) Held at 9° C. such extracts show a marked decrease in
peptic strength, corresponding to a 7-12 minute decrease in the
gelatine test at the end of 24 hours, more especially with the high
percentage of acidulation.

(d) Held at 20° C. (room temperature) practically the same
results are obtained in 6 hours as by holding 24 hours at 9° C.

(e) Held at 30° C. a still more rapid decrease in peptic strength
becomes apparent. The same results are obtained by holding
4 hours at this temperature as by holding 6 hours at 20° C.

(f) Held at 40° C. Holding at this temperature for 1 hour
is equivalent to holding at 30° C. 2 hours. The gelatine test
drops from 21 to 11 minutes.

(g) Held at 50° C. the gelatine test drops from 21 minutes to
5 minutes in 1 hour, indicating that the peptic activity is being
rapidly destroyed at this temperature.

(h) Held at 60° C. for 15 minutes, the gelatine test drops to 3 minutes, indicating that practically all of the proteolytic activity has been destroyed.

(i) Held at 70° C. for 3 minutes, the gelatine test equals 2 minutes.

These results indicate that temperatures of 50° C. or above exert a destructive influence on the proteolytic enzym.

III. Substitution of the bacterial acid by various other acids, mineral and organic.

In order to establish whether commercial lactic acid and various mineral acids (hydrochloric, phosphoric, sulphuric and sulphurous) and organic acids (tartaric and acetic) had an influence similar to that possessed by the bacterial acid prepared as already set forth, a set of experiments were made with a view of exciting peptic activity.

(a) The acids employed were used in the following concentrations; 0.5, 1.0, 1-1.2 and 2%.

(b) The temperatures of extraction were: 0°, 3°, 9°, 20°, 37.5° and 50° C. respectively.

Results: The following table gives the results of the gelatine test with various acids and degrees of acidulation:

Acidity	5%	1.0%	1.5%	2.0%
Bacterial lactic acid	6 min.	12 min.	15 min.	22 min.
Commercial lactic acid	1	2	2	2
Acetic acid	–	2	–	2
Phosphoric acid	1	1	1	1
Hydrochloric	2	4	5	5
Sulphuric	1	1	2	2
Sulphurous	1	1	2	2

Water extract (Acidity = 0%) gelatine test = 1 minute.

With the exception of hydrochloric and commercial lactic acid, these giving a slight increase in the gelatine test, the results were practically negative.

IV. The peptic strength of malts prepared from different types of barley.

The peptic strength of a large number of brewing malts received for investigation at the Wahl-Henius Institute was also deter-

mined, with special reference to the type of barley from which these had been prepared. These malts included low kiln dried or pale malts, brown or carmel malts, and black malts.

Results: These can be summarized as follows:

1. *Low kiln-dried or pale malts* prepared from

(a) Eastern, Manchuria, barley.

These showed the highest peptic strength, giving a gelatine test of from 14-25 minutes.

(b) Western, Bay Brewing, barley.

The peptic strength of these varies considerably with different samples, as is also the case with the Eastern malts, but as a whole the peptic strength of these malts is much lower, viz: Gelatine test 7-14 minutes.

2. *Carmel Malts.*

These have very little peptic strength. Gelatine test 2 minutes.

3. *Black or Color Malts.*

These have no peptic strength whatever.

GENERAL REMARKS

Moisture: The percentage of moisture seemed to effect the peptic strength. A number of samples containing from 2-3.9% moisture gave a gelatine test from 16-21 minutes; those containing a greater percentage of moisture had a considerably lower peptic strength, viz: Moisture 3.9%-6.4%, gelatine test = 7-12 minutes.

Yield: Malts with a higher yield also gave a higher gelatine test indicative of a higher peptic strength.

These results are significant, inasmuch as they show that malts prepared from Bay Brewing (Western) barley exhibit a lower peptic strength than those prepared from Manchuria (Eastern) barley.

THE BACILLUS VISCOSUS. ITS ACTION ON AMERICAN BEER AND ALE WORTS, BEFORE, DURING, AND AFTER THEIR ALCOHOLIC FERMENTATION

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The numerous investigations which I have made over a long period of time, and which I have endeavored to classify and briefly summarize, were originally prompted by certain developments in brewery practice, involving modifications in the nature of brewing materials. It had been suggested, and in many cases is still believed, that wheat and oat malts, when used as adjuncts to barley malt, may eventually cause trouble in our American beer, by favoring the development during and after alcoholic fermentation, of various types of organisms other than beer yeast. I allude specially to those types which produce in beers and ales the conditions known as viscosity, or " ropiness," and which have long been sources of annoyance in European breweries, where wheat or wheat malt enter into the composition of the grist. The " ropiness " of German " Weiss " beers, and of the Belgian spontaneous fermentation beers called " Lambic " and " Faro," is commonly attributed to the favorable nutritive medium created in the worts by the use of wheat, and one of the phases of this beer disease, which would be particularly obnoxious to our own brewers (who aim at producing beers and ales of great brilliancy) is that known as the " double face," a peculiar phenomenon which has been deeply studied by H. Van Laer, and ascribed by him to the action of Bacillus Viscosus Bruxellensis. You are aware, of course, that a number of viscous ferments are found in various branches of the fermentation industries. Pasteur describes one of them (a Streptococcus) in his " Etudes sur la Biere," and since then Kramer has isolated the " Bacillus Viscosus Sacchari," Glaser the " Bacterium Gelatinosum Betae,"

and Cramer the " Bacterium Viscosus Vini." Slime-forming bacteria of the Pediococcus type have also been separated by P. Lindner from Berliner Weiss Beer, and by Brown and Morris from English ale. The bulk of our knowledge of these organisms and their action, however, is derived from H. Van Laer who, working on three types—Bacillus Viscosus I and II and the Bacillus Viscosus Bruxellensis—has brought out many interesting facts, and among others, that all these ferments must necessarily commence their action on the constituents of the wort before the end of the primary fermentation; failing this, they are without effect on the finished products.

Up to the present time, the " ropy " ferments are practically unknown to our brewers, and my own practical experience with " ropy " beer in breweries, is limited to two cases. Both of them occurred in Canadian ales, and were induced by the action of a Pediococcus, entirely similar to that of Brown and Morris. It commenced its work in the original wort, and developed copiously during and after fermentation.

While I was investigating these cases, the questions that naturally arose were: (1) Which food bodies in the wort (nitrogenous or carbohydrate) are preferred and most easily attacked by different viscous ferments? And, (2) How may the action of the ferments be naturally controlled, or entirely inhibited? It is these questions that the results of my work are intended to answer, and in order to meet them rationally and practically, I have made all my experiments with the brewing materials customarily used in American practice, and with pure cultures of the Bacillus Viscosus Bruxellensis, obtained from the bacteriological laboratory of L'Institut Superieur de Brasserie de Gand, Belgium. In all cases, I have measured the viscosity produced by Van Laer's standard (i.e.), the time required in seconds for the passage of 50 cc of liquid through an opening of 3 mm in diameter.

After convincing myself that prolonged boiling of the worts with hops in varying proportions had no noteworthy influence on the growth and action of the Bacillus, I proceeded to make experiments in three series, " D " " E " and " F " to ascertain whether the nitrogenous substances or the carbohydrates in the

brewing materials are the more responsible for viscosity or "ropiness."

SERIES D: The carbohydrates used were 10 per cent. sterilized solutions in distilled water, of—dextrose—laevulose—saccharose maltose—lactose—raffinose—d.mannose—dextrine.   Of each of these solutions, a quantity of 50 cc was inoculated with a small platinum wire-loop of a 5-day wort-agar growth of Bacillus Viscosus Bruxellensis, the flasks being incubated at 25 C.   The laevulose—lactose—and   d.mannose   and   dextrine   solutions showed a viscosity of 50, 60, 50, 80 after twenty-four hours.   In the dextrose—saccharose—maltose—and raffinose solutions there were no signs of viscosity after 16 days incubation.

SERIES E: The solutions of this series were composed of 1 per cent. asparagin, 1 per cent. peptone (Witte) 0.5 per cent. of ammonium phosphate, 0.5 per cent. ammonium tartrate, and 0.5 per cent. ammonium nitrate, and yeast water.   After sterilization, 50 cc of each solution were inoculated and incubated at the same temperatures and in exactly the same manner as employed in *Series D*.   At the end of twenty-four hours, although development of the ferment had taken place, none of the liquids were viscous, but after seventy-two hours the yeast water and the solutions of asparagin and peptone showed a respective viscosity of 70, 80, and 62.   None of the inorganic nitrogen nutrients showed any signs of viscosity after two weeks incubation, and only a very slight development of the ferment took place in them.

SERIES F: The four sterilized carbohydrate solutions of Series D, which had not become viscous—dextrose, saccharose, maltose, and laevulose—were each treated with 0.5 per cent. ammonium phosphate, inoculated with the same amount of culture growth of the Bacillus, and all became viscous after twenty-four hours, the viscosity ranging from 60 to 65.

I conclude from the results of these three series of experiments that while the Bacillus Viscosus Bruxellensis contains Lactase, it does not contain Invertase or Maltase.   It cannot therefore attack Saccharose, Maltose, or Raffinose, and does not attack Dextrose.   In the case of Series F, the viscosity is due to the facility with which, under suitable conditions, micro-organisms form the enzymes that are needed for the purposes of their nutri-

tion. In the absence of nitrogenous matter, Invertase could not be formed in the solutions of Series D. If this conclusion is accepted, it follows that in a nutritive medium like normal beer wort, the Bacillus will exhibit no selection, and all the carbohydrates, and most of the nitrogenous substances, are equally susceptible to viscous fermentation.

The dextrine having produced the highest degree of viscosity in Series D, I made a further experiment, " G " to establish whether the conversion temperatures in the mash tun (or, in other words, the amounts of dextrines or malto-dextrines in a beer wort) have any influence upon the degree of viscosity that might be produced in a beer. Two worts were prepared from all barley malt, and two prepared from equal parts of barley malt and wheat malt. These worts were saccharified as follows: (1) all barley malt, saccharified at 62 C. (2) Barley malt and wheat malt, saccharified at 62 C. (3) All barley malt, saccharified at 73 C. (4) Barley malt and wheat malt, saccharified at 73 C. These worts were boiled with hops in the proportions generally prevailing in American brewery practice, and subsequently filtered and sterilized in Erlenmeyer flasks, the approximate specific gravity being, 1.040. 150 cc of each wort were inoculated with 1 drop of a 48-hour-old culture in wort of Bacillus Viscosus Bruxellensis. After 48 hours incubation at 25 C., the viscosities of all the worts were as follows: (1)—92. (2)—96. (3)—109. (4)—112. Judged from the standpoint of carbohydrate constituents, it becomes evident from these results that an increase of dextrines and malto-dextrines undoubtedly produces a proportionately higher degree of viscosity. Judged from the standpoint of nitrogenous constituents, on the other hand, the results seem rather contradictory, because we might expect a higher degree of viscosity in worts (1) and (2), from the facts of the lower conversion temperature of the mash, favoring a possible hydrolizing action by proteolytic ferments that could not act on the albumens at the higher temperature of 73 C.

My next two series of experiments show the influence of alcohol on the growth and action of the viscous ferments. One of them was conducted with barley and wheat malt wort of specific gravity 1.045, saccharified at 66 C., and the other with the resi-

dues from beer distillation, of specific gravity 1.025. Both media having previously been sterilized, alcohol was added to them in different amounts, ranging from 0.8 to 5 per cent., by weight, and portions of 50 cc each were treated with 1 drop of a 48-hour culture of Bacillus Viscosus Bruxellensis in wort. At the end of twenty-four hours incubation at 25 C., all the worts containing up to and including 3 per cent. of alcohol, were viscous, while those containing more than 3 per cent. of alcohol showed no viscosity, although development of the ferment had taken place. The beer distillation residues in the flasks containing up to and including 2 per cent. alcohol were viscous, and the flasks containing 2.4 per cent. of alcohol showed a growth of the ferment, but no viscosity. The flasks containing 3 per cent. alcohol showed neither viscosity nor development of the ferment. Judged from these experiments, the old-established fact is once more demonstrated, that the toxicity of poisons varies with the amount of nutritive media, and I believe it logically follows that under the conditions of nutrition existing in average American beers, an amount of 3.5 per cent. alcohol effectively checks the growth of viscous ferments. I have fortified this conclusion by a large number of tests, of which the following is an example:

A well known brand of American lager beer was selected, and found to contain 3.5 per cent. alcohol, and 5.2 per cent. of unfermented extract. The alcohol was distilled off, and the residue diluted back to its original volume. To one part of this diluted residue there was added 3.5 per cent. of ethyl alcohol, by weight, and thus three different media were provided: (1) The original beer, (2) The residue from distillation, diluted to its original volume, (3) The residue from distillation, containing 3.5 per cent. alcohol, by weight. After sterilization and cooling in hermetically sealed bottles, each sample was inoculated with 1 drop of a 48-hour culture of Bacillus Viscosus Bruxellensis, in wort. In 48 hours incubation at 25 C., experiment No. 2 showed a viscosity of 50, while Nos. 1 and 3 showed no development at all. After standing 8 days, the viscosity of No. 2 disappeared, whereas after standing for twenty days at incubation temperature, the samples 1 and 3 remained entirely unchanged.

I next made a series of experiments with worts and beers at

widely varying temperatures, and have proved that while low temperatures have a generally retarding influence upon the growth and action of the viscous ferment, both take place at 3 C. This fact being established, I conducted two series of experiments, in order to determine the action of the Bacillus Viscosus Bruxellensis under the varying conditions of wort composition, amount of pitching yeast, and temperatures of fermentation and storage, most common in American breweries. In both series, the same four different kinds of wort were employed, (i.e.): (1) Barley malt (2) Oat malt (3) Wheat malt (4) Barley malt, 60%—corn grits, 40%. The saccharification was effected at 68 C. in all cases, and the worts were boiled with the customary amount of hops. After cooling and filtering, the boiled worts were sterilized in flasks containing 500 cc each. The following were the gravities and viscosities:

(1)   Specific gravity, 1.039—viscosity, 15.
(2)   Specific gravity, 1.040—viscosity, 17.
(3)   Specific gravity, 1.039—viscosity, 16.
(4)   Specific gravity, 1.041—viscosity, 16.

I inoculated (C) the first series with 1 cc of a 48-hour culture of pure brewery yeast. Twenty-four hours later, I added to each flask 1 cc of a 48-hour culture of the Bacillus Viscosus Bruxellensis in wort. The fermentations were carried out at 17-19 C. Owing to the small amount of pitching yeast, active fermentation did not commence until the expiration of 48 hours, when the fermenting liquids all showed viscosity, ranging between 42-45. The microscope revealed a large number of healthy Bacillus Viscosus in all the flasks. After 6 days the fermentations were ended; the beers exhibited satisfactory clarification; the microscopical examination showed normal yeast cells with only a very small number of weak looking rods of the Bacillus Viscosus; and the viscosity had gone down to 19 and 21. The highest development of ferments, as well as of viscosity, was found in the oat malt beer. After filtration into sterilized bottles, hermetically closed, the four beers were stored away in a dark place at 18-25 C., and after six weeks, representative samples, carefully taken from each bottle, were found to be hazy, from albuminous bodies:

but with no sign of Van Laer's phenomenon of " double face." The viscosities were respectively, 17, 19, 18, 17, and only a trace of weak Bacillus Viscosus was present. At the end of three months, the beers were all examined again, and were found brighter, with the viscosities reduced to 16, 18, 16, 16, and with only minute traces of floating rod bacteria. The beer deposits all showed a rather large proportion of very weak Bacillus Viscosus, but less in the wheat-malt beer, and rather greater in that made from oat malt.

In the next series of experiments (J), with exactly the same kind of worts, I increased the amount of pitching yeast to 2 grammes for each 500 cc flask, and the fermentation was carried out at 10 C., with 1 cc of a 24-hour old culture of Bacillus Viscosus. Active fermentation commenced in 20 hours, and the fermenting liquids were examined microscopically every twenty-four hours. At no stage was there any more than a mere trace of rod bacteria, the largest number being always found in the oat malt. At the end of ten days the fermentations were finished, and the physical condition and the microscopical appearance of the beers and yeasts were recorded as follows:

<div align="center">SERIES J AT 10 C.</div>

	1	2	3	4
Viscosity,	15	16	16	15
Condition of liquid,	hazy	hazy	hazy	hazy
Microscopical appearance of beer,	weak yeasts with rods	weak yeasts more rods	As No. 1	As No. 1
Microscopical appearance of yeasts,	healthy, mixed with rods in all four.			

The beers having been carefully decanted off into two sets of sterilized bottles, were hermetically sealed. One set was stored at 10 C. and the other at 4.5 C., both for five weeks. At the end of this period, the bottles were opened and an examination made of the beers and deposits.

SET STORED AT 10 C.

	1	2	3	4
Viscosity,	16	19	17	16
Condition,	clear	hazy	fairly clear	clear
Microscopical appearance of beer,		Few yeasts and rods in all		

Microscopical appearance of deposit:

(1) Contained few weak yeasts and a small number of rods.
(2) The same as No. 1.
(3) Less rods than No. 1.
(4) The same as No. 1.

SET STORED AT 4.5 C.

	1	2	3	4
Viscosity,	16	18	19	16
Condition,	clear	hazy	clear	clear
Microscopical appearance of beer,		occasional yeast cells with weak rods in all		

Microscopical appearance of deposit:

(1) Weak yeasts, with rods.
(2) Same as No. 1.
(3) Less rods than No. 1.
(4) Same as No. 1.

I hope I have now made it clear from all these experiments that in my opinion the main factors governing the action of viscous ferments are (1) The amount and kind of pitching yeast used in the alcoholic fermentation; (2) The fermentation temperature and the attenuation of the beer; (3) The amount of acidity in the original wort.

As to the last point, H. Van Laer has covered it very fully and shown in his memoir, " Nouvelles Recherches sur les Fermentations Visqueuses "—1908, that an addition to the original wort of 0.15 per cent. H_2SO_4 will effectually stop the viscous action. In Experiment, Series C, where the fermentation was retarded by the very small amount of pitching yeast, the Bacillus Viscosus gained for a time the upper hand, while in Series J, carried out under exactly normal brewing conditions, the Bacillus

was uniformly kept in check. The growth and action of the Bacillus Viscosus being therefore controlled and determined by the amount of pitching yeast and the fermentation temperature, there is literally no danger from it under the conditions now existing and likely to exist in American breweries. Any rational and skillfully considered variations in the nature and kind of brewing materials, or in the methods of using them, are without practical significance.

THE COMPOSITION OF BREWERS' EXTRACT FROM THE STANDPOINTS OF CHEMISTRY AND BIOLOGY

By Doctor Francis Wyatt

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This paper has been prepared for the information and criticism of brewing technologists, and I dare to express the hope that its brevity, if not its merit, will commend it to your appreciation. Modern beer brewing, like all the other fermentation industries, has been elevated to the position of a science by the accumulated knowledge of intricate chemical and biological processes. From the manufacturing standpoint, beers are merely secondary products; the product first in importance in the brewery being a pure, uniform, and continuous culture of the Saccharomyces Cerevsiae, or yeast plant. On this line of reasoning, you must admit that uniformly successful and economic brewing operations must be based on the employment of brewing materials which, when properly blended and manipulated in the mash tub, will produce a nidus or pabulum propitious for the growth, activity, and devellopment of the ferment. Such a pabulum must have an acid reaction, and contain well defined proportions of readily fermentable sugars, readily assimilable protein and readily assimilable mineral salts, and it has hitherto, throughout the ages, been produced from that material which has furnished the foundation of all ales and lager beers, and given them their comprehensive name, Malt liquors. The most important cereal hitherto used in the production of malt is barley, and it has long been a matter of general knowledge that the chief difficulty with which the brewer of beer or ale has to contend in our country, is that of securing a sufficient supply of barley suitable for malting purposes. In the United States, the annual production of barley considerably exceeds 150,000,000 bushels of forty-eight pounds each, but the bulk of it is unfit for malting and the brewers and distillers are at pains to cover their needs of 75,000,000 bushels of malt at 34

pounds. The reason for this state of affairs is not for me to explain in this paper, but it is in one sense fortunate that the nature of our malts compels brewers' and distillers' technologists to use large quantities of such adjuncts as maize and rice; and, more recently, has attracted their attention to such other cereals for the manufacture of malt, as wheat and oats. I have lately devoted a great amount of study in the laboratory, as well as in the brewery, to the character and quality of wheat and oat malts, and I now invite you to discuss the conclusions I have drawn from the work.

The commercial malts used by the great majority of American brewers are chiefly made from the small and rather lean six-rowed barleys, grown in Wisconsin, Minnesota, Iowa, and Dakota; and it is only within the past two years that malts made from western red and white wheats, and from western white oats, have met with any recognition. I will clear the ground for what I have to lay before you by introducing at this point the average composition of types of all the cereals that may be used for malting, as shown by my analysis:

COMPOSITION OF AMERICAN BARLEYS, WHEATS AND OATS, TO BE

USED FOR MALTING PURPOSES

	Barley	Wheat	Oats
Moisture,	11.50	11.10	10.76
Fat,	1.96	1.85	4.29
Protein (Nitrogen x 6.25),	10.73	12.15	11.95
Fibre (husk),	5.28	2.22	11.80
Ash,	2.45	1.96	3.47
Carbo-hydrates,	68.08	70.72	57.73
	100.00	100.00	100.00

The general scheme adopted by commercial maltsters for malting these various cereals cannot be described in detail, but I believe that for present purposes, it may be sketchily outlined with sufficient exactitude, as follows:

GENERAL OUTLINE OF AMERICAN MALTING SYSTEMS

	Barley	Wheat	Oats
Temperature of steep water,	55 F.	55 F.	55 F.
Duration of steep (water being changed every 12 hours),	72 hours	34 hours	40 hours
Time allowed for germination at 65 F.,	7½ days	5 days	4 days
Time allowed for kilning,	2 days	1½ days	2 days
Initial kiln temperature,	80 F.	80 F.	80 F.
Final kiln temperature,	175 F.	165 F.	170 F.
Time for storage before use,	2 mos.	6 weeks	6 weeks

It is part of my professional duty to make daily analyses, and to keep constant watch and control over the malts, manufactured for brewers and distillers by various commercial maltsters throughout the country, from the cereals named, and by the methods outlined, and I have selected the following average types from my laboratory book, for the purpose of illustration:

	Barley	Red Wheat	White Wheat	Oats
Moisture,	3.70	5.15	5.20	2.90
Fat,	2.01	1.64	1.73	4.56
Protein (nitrogen x 6.25),	12.30	11.16	11.55	12.19
Fibre (husk),	7.12	3.14	3.26	13.40
Ash,	2.44	1.85	1.63	3.30
Carbo-hydrates, etc.,	72.43	77.06	76.63	63.65
	100.00	100.00	100.00	100.00

You will notice that the quantity of husk, or fibre, of the wheat malt is less than half that of the barley, whereas that of the oats is four times more than the wheat, and twice as much as the barley. To the practical brewer, who knows and understands that he is mainly dependent on the husk for the formation of an efficient filter bed in the mash tun, these differences will be of great significance. He will see at once that the lack of fibre in the wheat malts might restrict their use as adjuncts, because the drainage capacity of the mash is already tested to its utmost limit in American practice through the use of considerable pro-

portions of huskless raw cereals, and we already frequently encounter what is known as " set mashes." He will also not fail to see that the large amount of husk in oat malt provides an admirable offset to such a difficulty, and that while the addition of wheat malt alone, through its lack of husk, and in the absence of a filter press, causes considerable loss of time and extract by slow and imperfect drainage, the judicious admixture of oat malt ensures a porous filter bed and facilitates more complete removal of soluble extract than has hitherto been possible with any other kind of brewing material, and by our present systems of mashing and sparging. These are practical preliminaries, necessary in the preparation of my brief; and having disposed of them, I will now proceed to exhibit the three varieties of malt, from the standpoint of their chemical composition and brewing value, as found by miniature mashes in the laboratory of the National Brewers' Academy, according to the generally adopted rules of the Official Congress Method:

BREWING VALUE OF BARLEY, WHEAT, AND OAT MALTS
(MADE FROM CEREALS OF 1911 CROP)

	Barley	Red Wheat	Whte Wheat	Oats
Moisture,	3 70	5 15	5.20	2.90
Total available extract,	68 67	77 69	78 66	52 91
Total extract on dry basis,	71 30	81 96	82.98	54.49
Reducing sugar (as Maltose),	50 86	57 20	59.95	36.40
Total acidity (as Lactic Acid),	1 14	0 93	0 87	0 87
Ratio of sugar to non-sugar,	1:0 35	1:0 35	1:0 33	1:0.41
Soluble protein before boiling,	4 97	5 14	4.79	4.03
Soluble protein after 2 hours boiling, cooling, and filtering,	4.25	3.94	3 86	3.58
Soluble ash,	1 16	1 15	1 08	1.17
Soluble fat,	0 039	0 013	0.023	0.019
Color of 12° Balling wort, (Lovibond, ½ in. cell),	2 7	2 2	2.2	4.1
Drainage,	good	fair	fair	rapid
Break of wort, after boiling,	good	good	good	good
Physical condition,	crisp	crisp	crisp	crisp
Growth	full	full	full	full
Degree of mellowness,	92	94	96	93
Soluble protein after 2 hours boiling, cooling and filtering, (per cent. of dry extract),	6.19	5.07	4.90	6.72

While there is a very wide divergency in the extract yields of these malts, there is a great similarity in the main factors of their composition, especially in the radio of fermentable to non-fermentable carbo-hydrates, the total soluble ash, and the total acidity, estimated as Lactic acid. The noteworthy differences are in the soluble protein after boiling, and I hope you will agree that this chiefly concerns us because the nitrogenous bodies that are in real solution in the cold wort play the most important part in your yeast nutrition. I make this statement with diffidence, and I am not yet prepared to offer any satisfactory explanation of the respective parts played by the different varieties of protein in the yeast pabulum. I have, in fact, like all my predecessors, been unable to distinguish them in any other way than by their behavior under different methods of separation by various chemical reagents. I have devised and tried many promising schemes, but all of them have failed, and so I have been compelled to fall back on the established rule, and have termed albumoses or protooses those bodies which I have been able to precipitate by zinc sulphate, and I have classed as peptones those which I have precipitated by means of phospho-tungstic acid. The rest of the total soluble nitrogenous bodies I have grouped together under the terms amides and amino compounds and while I admit that this is vague, it will not be entirely meaningless to auditors of your experience.

DIVISION OF THE SOLUBLE NITROGENOUS BODIES IN BARLEY, WHEAT, AND OAT MALTS, ESTIMATED IN THE COLD, FILTERED WORT, AFTER TWO HOURS BOILING

	Barley	White Wheat	Red Wheat	Oats
Albumoses or proteoses,	1.01	1.59	1.67	1.07
Peptones,	0.40	0.51	0.53	0.60
Amides and amino compounds,	2.84	1.84	1.66	1.89
	4.25	3.94	3.86	3.56

The wheat malts contain by far the greater proportions of albumoses or proteoses, and this possibly accounts for what prac-

tical brewers describe as the " Fiery " or more violent nature of the fermentation of worts, in the preparation of which wheat malt preponderates, and undoubtedly explains the cloudiness of wheat beers and ales, up to the end of the primary fermentation. The barley malts, on the other hand, contain greater amounts of amides and amino compounds than any of the others, and thus we are brought face to face with the oldest and most perplexing of problems. If I have partially solved it to my own satisfaction, by hypotheses based on practical brewing and laboratory work, I cannot hope to make you entirely share my convictions. I nevertheless am firm in the belief that while non-precipitable crystalline, and readily dialysable bodies are in a truer state of dissolution in the pabulum, and therefore favor more vigorous fermentation, they do not favor cell growth. In all my own experiments, the bodies I have called albumoses or proteoses and peptones have proved effective yeast food; they are the first upon which the yeasts make attack, and undoubtedly cause a rapid multiplication of cells. I do not forget (and if I did, you would jog my memory) that the actual vital processes of yeast metabolism are entirely unknown to us. I recognize and agree that many synthetical as well as analytical changes take place in both yeast and pabulum, which we have no present means of investigating, but I am reasoning on facts, as I have noted and understand them, and I therefore repeat that in my experience, the proteoses and peptones have invariably behaved as highly nutritious and very exciting yeast food; and consequently I always make a point of limiting the quantities in which they are to be present in brewers' worts. Leaving this fascinating question for what is much more commonplace, because less obscure, I shall proceed to examine the soluble mineral bodies of the various malts, which I have found in the following proportions:

COMPOSITION OF THE SOLUBLE ASH OF BARLEY, WHEAT AND OAT MALTS

	Barley	Red Wheat	White Wheat	Oats
Silica,	0.020	none	none	0.070
Oxides of Iron and Alumina,	0.002	none	0.002	0.002
Lime,	0.001	0.001	0.002	0.003
Magnesia,	0.053	0.055	0.050	0 040
Potash	0.361	0.510	0.425	0.391
Soda,	0.020	0.018	0.017	0.018
Chlorine,	0.025	0.021	0.020	0.020
Sulphuric anhydride,	0 029	0.021	0.020	0.025
Phosphoric anhydride,	0.649	0.524	0.544	0 601
	1.160	1 150	1.080	1.170
Percentage of magnesia, in total ash,	4.57	4.78	4.63	3.41
Percentage of potash in total ash,	31.12	44.34	39.35	33.42
Percentage of phosphoric anhydride in total ash,	55.95	45.57	50.38	51.40

It is made evident by these tables that from the standpoint of soluble mineral constituents, all the malts we are considering are of equal value for the yeast, and being thus relieved of the necessity for speculation concerning them, I may pass on to the composition of worts prepared from these various malts. The mashes were made in accordance with the Official Congress Method, and the worts were boiled for two hours without hops:

COMPOSITION OF BOILED COOLED WORTS, PREPARED FROM BARLEY, WHEAT, AND OAT MALTS, COOLED TO 48 F., AND FILTERED

	Barley	Red Wheat	White Wheat	Oats
Indication by Balling,	12	12	12	12
Real Extract (by weight),	12.4	12.4	12.4	12.4
Total carbo-hydrates,	11.17	11.48	11.47	11.09
Reducing sugar (as Maltose),	9.22	8.90	9.00	8.52
Non-reducing carbo-hydrates,	1.95	2.52	2.48	2.57
Total acidity (as Lactic acid),	0.22	0.14	0.13	0.19
Total soluble protein,	0.767	0.628	0.607	0.833
Total ash,	0.21	0.18	0.17	0.27
Phosphoric acid,	0.115	0.080	0.083	0.131

The similarity in chemical composition of all these worts is, on the whole, remarkable; but the fact that most impresses me, and I feel sure will chiefly interest you is, that the wheat malts contain considerably less soluble nitrogenous bodies than either the barley or the oat malts. It is entirely contrary to the general supposition and belief, and proves very conclusively that if there be any objections to wheat malts as brewing materials, we must henceforth base them, not on the amount, but entirely on the nature of their soluble protein. My own brewery and laboratory work prove beyond a doubt that wheat malt contains too much albumoses or proteoses, and too little amides and amino compounds, and I have accumulated a mass of evidence, gathered on the large, industrial scale, in support of my deductions. Looking at the figures as they stand, however, it becomes quite evident that properly prepared malts from barley, wheat, and oats present only very slight differences from the chemical standpoint; and that by judiciously combining, or mixing them, a brewers' grist can be easily adjusted, to furnish a pabulum entirely propitious for the growth and development of normal beer yeast. I want to make it clear that the use of grists from such a mixture of malts will not only ensure the continuous purity and strength of yeasts, but will also enable the brewer to produce beers and ales of entirely normal composition; presenting no objectionable differences of flavor and aroma, and standing on a par, from every viewpoint, with any beers that might be brewed from the most faultless barley malt alone. In order to strengthen this conclusion, I shall next give you some interesting figures from working practice, which I have been permitted to take from the brewing books of some of my most important clients, but I must first ask your indulgence while I make a slight explanatory digression.

At the VII International Congress of Applied Chemistry, held in London in 1909, some of you may remember that I presented a paper, prepared in collaboration with Emil Schlichting, in which we demonstrated that owing to the nature of our barley malts, the most suitable pabulum for the growth and development of beer yeast, and for the assurance of continuous healthy and normal fermentations, in American brewing practice, was found in those worts in which the soluble, available protein (of the

nature and in the proportion I have set forth in the tables just presented) does not exceed approximately 4 per cent. by weight, of the solids in the cooled worts in the fermenting tuns. We pointed out the prominent defects in American barley malts which has forced us to this view, and we alluded to the unfortunate custom in America of drinking all beers—but especially those that are bottled—at abnormally cold temperatures. We explained that the high percentage of soluble nitrogenous bodies in malts forced us, in order to meet prevailing conditions, to reduce the albuminous matter in the worts to the necessary minimum, and we suggested that the best way of establishing a satisfactory balance was to so arrange the composition of the wort that from 30 to 35 per cent. of its total solids should be derived from a source containing practically no soluble nitrogenous bodies. What are known as Grits and Rice, pure commercial Starch, and Grape Sugar, are now in general use for the purpose, and in the choice of either material, the brewer is governed by individual preference, brought about by his practical experience. The remaining 65 or 70 per cent. of the wort solids have hitherto been obtained from barley malt and my present object is to show that extract of equal value may be furnished by mixtures of various malts, prepared from other cereals than barley. The mixtures must, of course, be made in such a manner as to ensure the presence in the solids of the cooled worts of approximately 4 per cent. of soluble, non-coagulable protein; 1 per cent. of total acidity, calculated as Lactic Acid; and a little over 1 per cent. of soluble mineral salts (apart from those derived from the brewing water). In other words, every 100 pounds of the solids of the wort (irrespective of its gravity, or of the amount of hops used in its preparation) must contain in addition to the properly constituted carbo-hydrates, very approximately the following vital constituents:

VITAL CONSTITUENTS OF 100 POUNDS OF DRY WORT EXTRACT

Total Acidity (as Lactic Acid),	1.00 per cent.
Albumoses or proteoses,	1.30 per cent.
Peptones,	0.50 per cent.
Amides and amino compounds,	2.20 per cent.
Potash (K_2O),	0 34 per cent.
Phosphoric acid (P_2O_5),	0.61 per cent.

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Having made this digression, I now present the brewery figures, promising only, that they are averages, and quite typical of a very large number of brewings during the past two years in breweries with which I am connected as Consultant. About half of the brewings were made from barley malt and rice only, and the other half from a blend of barley, wheat, and oat malts with rice; the proportions of rice being the same. The grists were made up from the following materials:

<div align="center">

SERIES A

BREWINGS FROM GRISTS COMPOSED OF BARLEY, WHEAT, AND OAT MALTS AND RICE

</div>

3,600 pounds western barley malt (brewery yield, 64.5 per cent. extract).

4,000 pounds oat malt, (brewery yield, 53 per cent. extract).

2,350 pounds wheat malt, (brewery yield, 75 per cent. extract).

4,200 pounds rice, (brewery yield, 80 per cent. extract).

Foundation temperature of mash,   100 F.

Saccharification temperature, held 25 minutes,   155-156 F.

200 pounds Hops ($\frac{1}{2}$ Pacifics, $\frac{1}{2}$ N. Y. States)

Amount of cooled wort collected in fermenters,   300 barrels

Gravity of cooled wort,   12 B. (sp. gr. 1.049).

<div align="center">

SERIES B

BREWINGS FROM GRISTS COMPOSED OF BARLEY MALT AND RICE ONLY

</div>

9,922 pounds western barley malt, (brewery yield 64.5 per cent. extract)

4,200 pounds Rice, (brewery yield 80 per cent. extract)

Foundation temperature,   100 F.

Saccharification temperature, held for 25 minutes,   155-156 F.

200 pounds Hops ($\frac{1}{2}$ Pacifics, $\frac{1}{2}$ N. Y. States),

Amount of cooled wort collected in fermenters,   300 barrels

Gravity of cooled wort,   12 B. (sp. gr. 1.049).

The chemical composition of these cooled filtered worts, as shown by the average of 52 analyses of samples taken from the fermenting tuns of the brewery by one of my assistants, is as follows:

COMPOSITION OF BREWERY WORT

	Series A.	Series B.		
Indication by Balling,	12	12		
Real Extract (by weight),	12.40	12.40		
Reducing sugar (as Maltose)	8.61	8.58		
Total acidity (as Lactic acid),	0.13	0.14		
Ratio of sugar to non-sugar,	1:0.44	1:0.44		
Albumoses or proteoses,			0.16	0.13
Peptones,			0 06	0.05
Amides and amino compounds,			0.30	0.35
Total protein insolution,	0.52	0.53		
Total ash,	0.18	0.17		
Potash (K₂O),	0.042	0.039		
Phosphoric acid (P₂O₅),	0.075	0.077		

It is proper (although perhaps unnecessary) to explain that, included in the protein figure of both these analyses, there is a very minute quantity of nitrogenous matter, derived from the hops; but the quantity is so small that I have taken the liberty of regarding it as negligible, since it could have no bearing whatever on the issues involved in this paper. I have also neglected, as likely to lead to some confusion, any constituent of the total ash that may have been derived from the brewing water.

The materials used in all the breweries which have furnished these figures have been carefully tabulated, and compared with the chemical analyses of the malts, the rice, and the worts, and this has enabled me to establish the composition of the actual dry, solid extracts of the worts of Series A and Series B, as follows:

COMPOSITION OF DRY EXTRACTS OF WORTS

SERIES A

Extract derived from malted western barley,	24 per cent.
Extract derived from malted oats,	24 per cent.
Extract derived from malted wheat,	18 per cent.
Extract derived from rice,	34 per cent.

COMPOSITION OF DRY EXTRACTS OF WORTS
SERIES B

Extract derived from malted western barley,   66 per cent.
Extract derived from rice,   34 per cent.

The gravity, color, flavor, and appearance of all the worts from Series A and B were approximately identical. They ran clear, free and bright through the filter bed, at the rate of from 80 to 90 barrels per hour, and they were cooled to 48 F. and mixed with yeast, in amounts calculated to 3 per cent. on the solids. The fermentation ranged in each case up to 55 F., and was entirely finished in nine days. The yeast settled well, and the crops in all cases were approximately 4 to 1. The beers ran from the fermenting tuns into settling tanks at a temperature of 32 F. At the end of two weeks they were sent into chip casks; treated with 12 per cent. of krausen from similar brewings; fined, bunged, and kept under pressure for six weeks, when they were filtered, and racked off into trade packages, or bottled and Pasteurized and sent out for consumption in the regular manner.

I have collected a number of analyses of these finished beers, from samples taken by my assistants at the breweries at the time of racking, and I offer the following typical examples for your consideration:

	A	B
Original Gravity (by Balling),	12.05 B	12.05 B
Present Gravity (by Balling),	3.8	3.7
Carbonic acid gas,	0 37	0.35
Absolute Alcohol (by weight),	3.53	3.47
Volatile acidity (as Acetic Acid),	0.06	0.07
Unfermented solids,	5.51	5.63
Reducing sugar (as Maltose),	1.72	1.82
Fixed acidity (as Lactic Acid),	0.14	0.16
Total protein,	0.33	0.37
Ash,	0.19	0.19
Real Degree of Fermentation,	55.5	54.6
Albumoses or proteoses,	0.081	0.076
Peptones,	0.048	0.051
Amides and amino compounds,	0.201	0.243

Thanks to the significance of all my figures, there is very little left for me to say, and I shall therefore merely formulate my conclusions, which are:

(1)   That the chemical composition of beers brewed from a combination of malted barley, malted wheat, malted oats, and rice, and that of those brewed from barley malt and rice only, with the same proportions and qualities of hops, and by the same mashing, boiling, cooling, and fermenting processes, is identical.

(2)   That the biological condition, and the aroma and taste; the brilliancy of appearance, and the capacity for holding a good, lasting foam, are also identical.

(3)   That no difference can be detected in any of these beers, either by the eye, the nose, or the palate, even after they have been Pasteurized and exposed to low temperatures.

If I have sufficiently excited your curiosity and interest, my work may arouse through you the dormant faculty of adaptation in the practical brewers. If the captains of our industry once fairly realize the bearing and importance of the large and successful experiments I have related, they will understand without difficulty the means they offer of emancipation from slavish thraldom to the barley dealers, and ultimate practical independence of all incidents that may at any time arise to disturb the barley market.

I offer my sincere thanks to my colleague Emil Schlichting, and to his various assistants, for the valuable and diligent work they have done for me in the chemical and biological Laboratories.

RECENT PROGRESS IN THE STUDY OF YEASTS AND FERMENTATION

(Continued from the VII International Congress held in London, 1909)

By Francis Wyatt, Emil Schlichting, and H. Winther

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General Character and Properties of Yeast

F. Schoenfeld, writing of top fermentation yeasts (Wochenschr. fur Br. 1909), finds that the characteristic property of going to the surface can be lost, and is not restored by the usual means of warm fermentation or addition of sugars. By cold storage, however, this property can be accelerated, and better results were obtained by this treatment from high fermenting yeasts than from low fermenting species.

A yeast in which the properties of top fermentation are more pronounced than those of bottom fermentation, can be brought to ferment " up " by the addition of light, porous substances. The tendency to form lumps, as by bottom yeasts, is increased by cold storage, which therefore acts in two ways, developing both the properties of a bottom yeast and of a top yeast: A warm fermented yeast is generally of a "dusty character." The cultivation of absolutely constant bottom fermenting yeasts is practically impossible.

A. Harden and R. Jones (Proc. Roy. Soc., London, Series B.) have demonstrated that Saccharomyces Carlsberg I, which, under ordinary conditions does not ferment galactose, can acquire this property by cultivation in a medium of yeast water, containing 20 per cent. of hydrolized lactose and 0.15 per cent. $K_2H PO_4$. Galactose can also be fermented by the juice expressed from a yeast cultivated in this medium; the fermentation being assisted by the addition of phosphates, and also by very small amounts of Na_3AsO_4. In the opinion of R. Kusserow (Journ. Inst. Brewing, 1911) there exist two physiologically different varieties of yeast,

one of which causes fermentation, while the other, consisting of the long cells produced by strong aeration, absorbs oxygen and does not cause fermentation. The same author states that by cultivating bottom yeast for three or four generations in a lactic acid mash at 20–24 R., it may—after some days—completely assume the character of a top yeast. F. Schoenfeld and H. Rossmann have studied the behavior of top fermenting beer yeasts in the second and third generations, in order to determine whether these generations show the characteristics which are generally considered typical for top yeasts (i.e.): (1) Branched, budding formations; (2) Little fermentation of melitriose; (3) Formation of surface yeast at room temperature; (4) Milky mixture in water; and conclude that yeasts which at the time of isolation show the production of surface yeast, also inherit all the characteristic properties, while yeasts which do not show surface growth differ in the other respects, all giving, however a milky mixture with water. The other properties are latent, and may be brought out by certain treatment.

CONSTITUENTS OF YEAST

It has been stated by Henneberg (Wochenschr. fur Br., 1910) that the amount of glycogen contained in yeast neither indicates the condition of the cell, nor illustrates the composition of the nutritive medium. Inorganic ammonia salts and peptones stop the formation of glycogen, and gypsum is unfavorable for its formation. Yeasts rich in protein (above 53%) contain very little or no glycogen, which explains the fact that yeasts from potato, and other concentrated mashes, contain very little glycogen. Buchner-Haehn (Biochem. Zeitschrift, 27) have found that during storage in water only a small amount of phosphor-compounds are extracted from living yeast. Nevertheless the juice from yeast stored in this manner contains less phosphorus than juice from fresh yeast, and has less fermentative power. Acetone yeast yields all the co-enzyme to cold water, and can be regenerated by the addition of yeast water. Out of 1.19 grm. P_2O_5 found in 100 grm. yeast, only 0.37 grm. can be detected in the press juice. Acetone "lasting" yeasts contain a larger amount

of phosphorous than those prepared with ether, indicating the extraction of some phosphor-compounds by the ether.   In these lasting yeasts, there is no relation between the contents of phosphorus and the fermenting power, the latter depending on the consistency of the extracted juice, and the amount of precipitate produced by acetone.   E. Salkowski (Chem. Centralblatt, 1911) has found that pressed yeast contains 5.39 per cent. yeast-gum, and of this about 5.5% is soluble.   The gum does not reduce Fehling's solution.   Th. Bokorny, (Allg. Br. Hopfzeit. 1912) concludes, from observing certain micro-chemical reactions, that the potassium in the yeast cell is present as soluble salts in the sap, and possibly as potassium albuminate in the protoplasm and nucleus.   Henneberg distinguishes between albumen yeasts, glycogen yeasts, and fat yeasts, and states that yeasts containing more than 60 per cent. albumen are over fed.   He divides the fat-yeasts into two distinctly different groups, *reserve* and *degenerate*. Yeasts from cask sediments belong to the first group, and starving and over-aerated yeasts belong to the second.   According to Levene (Biochem. Zeitschrift, 1909) yeast nucleic acid is identical with Osborn and Harris tritico-nucleic acid.   After studying the differences in the chemical composition of " dusty " yeasts and " lumpy"' yeasts, Schoenfeld and Hirt find that the last named contain a larger amount of albumen inorganic constituents— phosphoric acid and magnesium—but a smaller amount of glycogen, than the "dusty" yeasts.   A. Fernbach and Vulquin (Annal de la brasser et de la dist) have found that by extracting a yeast dried at 70 C. with weak hydrochloric acid, they obtain a liquid which, after being made slightly alkaline with soda, gives a distillate—in vacuum at 35 C.—very poisonous to Logos yeast.   By a similar treatment, they obtained crystalline chlorine-hydrates, which also act as poisons for Logos yeast, and give reactions similar to the amines.   If a yeast which has been standing at room temperature for several days is used for the extraction, no toxic action is shown by the distillate.

ENZYMES AND THEIR ACTION

F.   Resenscheck (Biochem.   Zeitschrift) states that if yeast juice is precipitated with colloidal iron-hydrate and then filtered

it suffers great loss of fermenting power. The precipitate will not provoke fermentation, but it has a similar regenerating action to yeast water upon weakened yeast juice. He concludes that the precipitate is an absorption compound between iron hydrate and the co-enzyme of yeast juice. E. Buchner and H. Haehn (Biochem. Zeitschrift, 1909) have studied the relations between yeast-press juice and yeast water, and find that the regenerating action (restoration of the co-enzyme) of yeast water upon yeast juice, which has carried out one fermentation, is inconstant. When the yeast water is added three days after the fermentation, the regeneration is always complete, but after four or more days, it is very doubtful; owing to the destruction of the zymase by the endotryptase. The fact that zymase is left in the juice after fermentation is explained by the protective action of the co-enzyme against the endotryptase. The greater the amount of co-enzyme, the longer zymase remains active. Addition of glycerine retards the destruction of the yeast juice, and the addition of 5 per cent. soda-phosphate preserves the fermenting power of the juice. Potassium carbonate, in the proportion of 2.5 per cent. protects the zymase, but destroys the co-enzyme. Repeated addition to yeast juice of yeast water, without any sugar, protects the zymase, and the juice will remain active for from two to four days. The theory previously advanced by Buchner-Klatte, that the lipases are responsible for the destruction of the co-enzyme, has not been experimentally proved; and the authors are of the opinion, that the co-enzyme is an easily saponified organic phosphoric acid ester. They also find that (Biochem. Zeitschrift, 1910) yeast water, besides protecting the enzymes, also protects the coagulable albumens against the action of endotryptase, and gather from this that zymase is of albuminous nature. Yeast water contains an agent which acts as a general protector against all proteolytic enzymes, and the authors name this, *Antiprotease*. If their conclusions are correct, the regeneration of yeast juice by yeast water is not due to the presence of co-enzyme, but depends upon the action of *Antiprotease*. Both the co-enzyme and the Antiprotease are destroyed by Vicinus Lipase. Antiprotease is an organic, hydrolizable body of estery composition: it can also be extracted from

acetone-lactine yeast by cold water, and probably plays an important part in the yeast metabolism. M. N. Straughn and W. Jones (Journ. Biol. Chemist., 1910) have definitely proven that yeast contains the nucleic-ferment, guanase,which changes guanin into lanthin, and A. Harden and W. Jones, (Proc. Roy. Soc., 1909) have shown that yeast juice acts upon and ferments mannose in the same way as it does glucose, both in the absence and presence of phosphates. In the presence of phosphates laevulose is fermented more rapidly than the other sugars, and requires a higher optimum amount of phosphorous. Bretton (Compt. rend. de l'acad. des Sciences) has found in extracts from top yeast an enzyme, which is not found in extracts from bottom yeast, and which hydrolizes methyl-glucose. Its optimum for action is 30 C., and it is killed at 45 C. Salkowski (Chem. Centralblatt, 1909) has found that invertase can be extracted from pressed yeast with cold water, and that at 40 C. it is able to produce 160 times its own weight of invert-sugar. At 40 C. yeast invertase remains active, even when the yeast putrefies. A. v. Lebedew (Zeitschrift physiolog. Chem., 1911) has extracted the active fermenting enzymes from the yeast cells, by simple maceration of dried yeast with water at 25–30 C., and finds that this yeast extract is more active than the press-juice. E. Kayser (Chem. Central Bl., 1911) claims that Lebedew's yeast juice is benefitted by manganese phosphate and nitrate, as well as by potassium phosphate. J. van Anstel and G. van Hersen (Konink. Acad. v. Wetens., Amsterdam) have examined the theory of Duclaux and Blackmann, concerning the optimum temperatures for enzymic action, which is, that the velocity of action is increased constantly with increasing temperature, but that simultaneously an increasing destruction of the enzyme takes place. The increase in velocity itself, however, always follows the rule of Van t. Hoff. They have made exhaustive investigations of the alcoholic fermentation and the inversion of cane sugar, determining the relation between the velocity of action, the temperature, the time, the yeast, and the sugar concentrations. They find that the deviation from the Van t. Hoff's rule increases with increasing temperatures. They also find that the velocity shows for the time, O; a decided temperature optimum, and conclude

that, above the optimum temperature, there occurs a correspond-
ing inactivity of the enzyme.   They disagree with H. Euler's
theory that the enzymes are rendered somewhat inactive below
the optimum temperature.   H. Euler-Ugglas, (Archiv. f. Kemi
-3) have made experiments to produce increased amounts of cer-
tain enzymes from certain micro-organisms. They show that a
yeast cultivated under certain conditions in a solution containing
4.5 per cent. glucose and 5.9 per cent. peptone, contain only
half the amount of invertase found in a yeast cultivated in a
solution of 4.5 per cent. cane sugar, and 5.9 per cent. peptone.
The same authors (Zeitschrift physiol. chem. 1911) have worked
out that the velocity of reaction of the extract from a " lasting "
yeast gives a measure of the activity of the soluble enzymes of the
yeast.   They find that extract from "lasting" yeasts which,
previous to drying, was treated with 0.3 per cent. solution of
sodium phosphate for 40 minutes, is inverted 2.7 times as quickly
as the extract from a yeast not treated in this way, and suggest
that the effect of the phosphate treatment upon the invertase is
largely dependent upon the condition of the yeast before the
treatment.   These conclusions are not confirmed by E. Lindberg,
who finds less rapidity of action by the use of sodium monophos-
phate in solutions of 0.5 per cent. to 2 per cent.   The zymase
in " lasting " yeast is to a great extent made inactive by the proc-
ess of preparation.   H. Euler and S. Kullberg (Zeitschrift.
physiolog. chem., 1911) express the following views on the nature
of enzymes: Unlike zymase, invertase seems to be independent of
the protoplasm.   Inversion takes place much more rapidly than
fermentation; the proportionate value between the inversion fac-
tor and the fermentation factor of a bottom yeast in a 16 per cent.
saccharose solution is 370.   This value seems to be a constant
characteristic for each different yeast race, but varies with the
sugar concentration.   As the relation found between the inver-
sion factor and the sugar concentration is the same for all enzy-
mic actions it must be assumed that the sugar concentration
is the same inside the cell as outside in the fermenting liquid, and
hence the conclusion that a " lasting " yeast prepared by proper
drying, gives a qualitative, but not always a quantitative, idea
of the enzymes in the living yeast.   The same authors (Zeit-

schrift physiolog. chem. 1911) have studied the enzyme phosphatase, which is the agent producing the carbo-hydrate-phosphoric-acid-ester in the second phase of Iwanoff's fermentation theory, and they find that it has only a synthetizing action and this action is continued until all the phosphate ions have disappeared. Phosphatase is destroyed by heating to 60 C. for 30 minutes; it acts best in slightly alkaline solutions. The esters formed by the phosphatase from dextrose, laevulose and saccharose are optically inactive. In the formation of the carbohydrate-phosphoric-acid ester, probably two enzymes are involved; one which transforms the original sugar into the ester-forming carbohydrate and the other which, from this, forms the ester itself. In a subsequent work, H. Euler and H. Ohlsen (Zeitschrift physiolog. chem. 1912) have related their experiments to determine the factors which influence the formation of the carbohydrate phosphoric-acid-ester. They find that with increasing amounts of phosphates, the velocity of formation decreases, whereas by the addition of an ester-salt, it is accelerated. The sodium salt of the carbohydrate-phosphoric-acid-ester acts as a catalytic agent during fermentation, and according to Iwanoff is probably identical with, though much stronger than, the co-enzyme of Harden and Young. According to A. V. Lebedew (Chem. Centrallblatt, 1911) the zymase in maceration—yeast juice—is a typical enzyme. The amount of sugar fermented is approximately proportional to the amount of co-enzyme, when the proportion of the latter in the juice exceeds a certain limit. The fact that yeast is more active than yeast juice is explained by the power of the yeast cell to synthetize new co-enzyme co-incidentally, and at the same rate, at which it is destroyed by the fermentation. The same author has shown (Biochem. Zeitschrift, 20) that by the fermentation of sugar with press-juice, a certain amount of the sugar disappears without any corresponding production of CO_2; exactly as in the case of a mixture of glucose solution with press-juice from which the co-enzyme has been separated by filtration through Bechhold's Collodium filter. Press-juice, free from glycogen, contains two hydrolizable sugar compounds; one which is free from, and the other which contains phosphorous. The last is probably the co-enzyme of zymase,

and is likely to be an intermediate product in the formation of alcohol and CO_2 from glucose. From the exhaustive experiments of Euler and Kullberg (Zeitschrift physiolog. chem. 1911), it appears that a great difference exists between the properties of the enzyme Zymase, (in a broad sense), Maltase, and Invertase, the first and second named being considerably weakened by the action of antiseptics and by drying, while the yeast invertase is scarcely susceptible to these influences. It is inferred from this that the yeast enzymes are originally parts of the plasma, and are either separated from it in the living cell (in which case they are easily extracted) or are only separated after the plasma is killed. Dried yeast, produced after preliminary treatment with a 2 per cent. solution of KH_2PO_4 is weaker than a yeast dried without treatment. E. Navassart (Chem. Centrallbl., 1911) has made experiments on the action of the tryptic enzymes in yeast, and has shown that it is not accelerated by the presence of certain concentrations of antiseptics, and that 1 per cent. formaldehyde stops the autolysis. Compared with the action in chloroform water, the action of nuclease is increased in $\frac{1}{4}$ saturation of mustard oil water.

THEORIES OF FERMENTATION

L. Iwanoff (Centralblatt f. Bacteriolog., 1909) has made extensive studies of organic phosphor combinations during the fermentation, and has reached the conclusion that in the case of glucose, there is: (1) Depolymerisation of the glucose; (2) Combination of the depolymerisation products with phosphoric acid by the action of an enzyme, Synthease; (3) Splitting up of the thus formed triosophosphoric acid by alcoholase into alcohol and CO_2. In opposition to this theory, Harden and Young, (Centralblatt f. Bacteriolog., 1910) agree that the hexosephosphoric acid (Iwanoff's triosophosphoric acid) is not an intermediate product of the alcoholic fermentation, but actually accompanies the production of alcohol. They consider the hexosephosphoric acid a fermentation by-product which, however, is again hydrolized into fermentable sugar and phosphate; this process going on continually as long as fermentable sugar is present. When the

alcoholic fermentation ceases, the phosphates start to accumulate. The same authors disprove the presence of Iwanoff's Synthease, by showing that while washing of Zymin with water renders it inactive as a ferment, its activity can be restored by addition of the *boiled* wash water. R. Kusserow (Centralblatt f. Bacteriolog. 1910) has formed a theory of the alcoholic fermentation, which briefly is, that (1) The yeast, poor in oxygen, reduces one part of the sugar to a diatomic alcohol; (2) This diatomic alcohol breaks up into ethyl alcohol, CO_2, and hydrogen; (3) The hydrogen, in *statu nascendi*, reduces another part of the sugar (as mentioned under I) and thus completes the cycle. According to Lebedew (Compt. rendu Acad. des sciences 1–53), in the fermentation of any sugar, the first product formed is a phosphoric-acid-ester, during the hydrolisis of which alcoholase splits it into alcohol and CO_2 the hydrolysis of this ester is consummated within a measurable time, but the action of the alcoholase is almost instantaneous, rendering it impossible to detect any intermediate products without the aid of a retarding catalytic agent. Another theory of interest is that of Walter Loeb (Biochem. Zeitschrift, 1910) who believes that from the hexoses are first formed trioses, and that these are either first changed into lactic acid or directly broken up until the final products are alcohol and CO_2. Assuming that dixoyacetone is an intermediate product, Loeb believes that this is changed into glycolic-aldehyde and formaldehyde, and these further into alcohol and CO_2. E. Buchner and Mersenheimer (Chem. Zeitschrift, 1910) deny that lactic acid is an intermediate product of the alcoholic fermentation, on the ground that it is entirely unfermentable by living yeast; and that the small amount of it formed during fermentation is possibly produced from the dioxyacetone. This work disproves the theory of Schade, that lactic acid is first formed from the sugar, and then transformed into acetaldehyde and formic acid, which then produce the alcohol and CO_2. The authors believe that dioxyacetone is the intermediate product of the alcoholic fermentation. H. Euler and G. Lundequist (Chem. Centralbl., 1911) advance the opinion that in the fermentation of maltose, the CO_2 formed in the first half of the reaction is proportional to the time consumed, and that maltose is fermented almost as

quickly as glucose. The hydrolysis of the maltose takes place almost simultaneously with the fermentation, very little of the hydrolyzing products being detectable at any stage. The fermentation of mannose is slower than that of glucose, and is not influenced by monosodium phosphate.

PRODUCTS OF FERMENTATION

F. Ehrlich (Biochem. Zeitschr., 1909) is of the opinion that succinic acid is the product of the albuminous metabolism of the yeast; glutaminic acid being the starting point for its formation. Olive Evelin Ashdow and John Theodore Hewitt (Journ. Chem: Soc., London, 97) have studied some of the by-products of the alcoholic fermentation, and reached the conclusion that acetaldehyde is a product of an action of the yeast upon the sugar. The largest amounts of acetaldehyde and alcohol are formed when alannin is the source of nitrogen; when the yeast draws only upon its own nitrogenous constituents as the source of nitrogen, a very small amount of acetaldehyde is formed, and at the same time the formation of higher alcohols is increased. The authors believe that alannin is possibly an intermediate product of the alcoholic fermentation formed from dioxyacetone, and base their hypothesis on the facts that Drechsel has decomposed alannin into acetaldehyde, carbon-monoxide and ammonia; and that Schade has produced alcohol and carbon di-oxide from acetaldehyde and formic acid. In opposition to this view, Buchner and Mesenheimer point out that a mixture of acetaldehyde and formic acid is not fermentable; and that there is a notable decrease in the amount of acetaldehyde when formic salts are added to the fermenting liquid. C. Neuberg and A. Hildesheimer (Biochem. Zeitschr., 31) state that the soluble salts of acetyl-carbonic acid, the transformation product of methyl-glyoxal, give, by fermentation with yeast, a considerable amount of CO_2, but no ethyl alcohol. That substances not belonging to the carbohydrate group, will produce CO_2 by fermentation, is a fact to be considered in judging the usual fermentation tests for sugar. C. Neuberg and L. Tir. (Biochem. Zeitschr., 32) have demonstrated the fermentability of the following substances in solutions of 1% to

3%, the acids being used preferably in the form of potassium salts, Formic acid, acetic acid, butyric acid, glyoxalic acid, d-tartaric acid, lactic acid, malonic acid, citric acid, acetyl-carbonic acid, l. b. oyx-butyric acid, glycerin-phosphoric acid, glycerin-ethylene-glycol, d. l. alanin. None of these fermentations are dependent upon the life-action of the yeast cell; the gas developed is always CO_2 and the phenomena are possibly related to the respiration of the yeast. C. J. Lintner and H. J. v Liebig (Zeitschr. physiolog. Chem., 1911) have studied the changes undergone by furfurol during fermentation, and come to the conclusion that it is changed into furylic alcohol, both by fermenting yeast and by yeast mixed with water. 70 per cent. of the furfurol is changed into furylic alcohol, and 30 per cent. into a crystalline body. Matthieu (Allg. Br. Hopfzeit, 1912) points out that the formation of mercaptane during the alcoholic fermentation is brought about by the action of the yeast upon sulphates and sulphites; increasing with higher temperatures, and strongest with sulphites and sulphurous acid, after the main fermentation. K. Neuberg and L. Karczag (Biochem. Zeitschr., 36) have made experimental fermentations of acetyl-carbonic acid, d-tartaric acid, and glycerin-phosphoric acid, and have found that all of them not only produce CO_2, but disappear from the fermenting liquid. C. J. Lintner states that the presence of furfurol in the wort can be traced back to the pentosans in the husk of the barley. As most yeasts form H_2S during fermentation, this will act upon the furfurol and form polythio-furfurol. Hartwig Franzen (Wochenschr. f. Brauerei, 1911) has found that during fermentation of a wort containing formic acid, certain species of yeast cause it to disappear, while at the same time, re-formation of formic acid goes on. This formic acid, thus produced, is not a fermentation product of the amido-acids, but must be considered an intermediate product in the alcoholic fermentation proper. The same processes also take place when using yeast juice in place of yeast. C. Neuberg and L. Karczag (Biochem. Zeitschr., 1911) have shown by experiment that the sugar-free fermentation is most easily carried out with the potassium salts of acetyl-carbonic acid, or oxy-maleinic acid, both of which produce pure CO_2 gas. By the fermentation of one per cent. solutions of the pure acids,

acetaldehyde is formed; the active enzyme in this fermentation is called, Carboxylase. Diana Bruschi (Atti R. accad. dei Lin: Roma, 1912) is of the opinion that the formation of glycogen is dependent upon the function of the living cell. L. Karczag (Biochem. Zeitschr., 1912) has made a study of the behavior of yeast toward the stereo-chemically different tartaric acids, and finds that the d-tartaric acid produces more CO_2 than the l-acid; the d-l-acid produces less CO_2 than the d-acid, but more than the l-acid; the meso-tartaric acid produces the same amount as the d-acid. Th. Bokorny (Chem. Zeitung., 1910) states that the glycosides are not fermentable. After ten days standing with emulsion, he, however, noticed a fermentation of the hexose formed. Buchner and Mesenheimer (1910) attempt to disprove the theory, that the glycerine formed during fermentation is a decomposition by-product of the albuminous substances. Th. Bokorny (Chemikr. Zeitg., 1910) writes on the relation between the pentoses and the formation of glycogen, and shows that by the use of a very small amount of yeast, glycogen is formed in presence of both Xylose and arabinose. Neubauer and K. Fromherz (Zeitschr. phisiolog. Chem. 1911) have studied the transformation of the amino-acids during fermentation. Ehrlich has stated that the fermenting yeast transforms the amino acids into the alcohol containing one C-atom less than the amino-acid transformed. The authors' experiments prove the presence of a keton-acid as an intermediate product in this transformation: Part of this Keto-acid oxy-phenyl-glycolic acid, is further reduced by the fermenting yeast into l-phenyl-glycolic acid. The authors also assert that the yeast is able to produce the opposite reaction, the oxidation of l-phenyl-glycolic acid into the corresponding oxy-acid. By the fermentation of p-oxy-phenyl-acetyl-carbonic acid, large amounts of p-oxy-phenyl-ethyl alcohol are formed.

The Nutrients of Yeast

Heinrich Zikes (Sitzungsbericht Akd. d. Wiss., Wien) describes a species of Torula isolated from laurel leaves, which is able to assimilate nitrogen from the air; the amount assimilated being 2.4–2.3 mg. for 1 gram sugar fermented. He states that several species of Willia and Pichia grow very well with the

atmosphere as sole source of nitrogen. P. Lindner (Wochenschr. f. Br., 1911) has demonstrated the important fact that yeast is able to assimilate ethyl alcohol and use it as a source of nourishment. M. Ruhner (Chem. Centrallbl.) sets forth that the assimilation of nitrogen is regulated chiefly by the relation of the nitrogen in the medium to the nitrogen in the cell; if the amount of nitrogen in the medium is small compared to the amount in the cell, no growth will take place, the yeast only accumulating reserve food. W. B. Crosz and B Tollens (Journ. f. Landwirtsch., 1911) have found that pentosans can be used as yeast foods, but only in liquids which contain solely artificial nutrients. In certain cases, from nine to fifteen per cent. of the pentosans were used up, forming alcohol and lactic acid, besides acting as yeast food. T. Takahashi and T. Yamamoto (Wochenschr. f. Br.) call attention to the statement of Kusserow, that the decomposition products of proteins are more easily assimilable than the proteins themselves, and to that of Stockhauser, that the assimilation of the products of antolysis is dependent upon the yeast species. The authors find that the amount of amino acids assimilated by Saki yeast varies at from 0.004 to 0.064 per cent. and is dependent upon the yeast race, and they state that all nitrogenous substances, except Tyrosin, Cystin, nitrites and nitrates, are easily assimilated by Saki-yeast. H. Will and R. Hensz. (Zeitschr. f. ges. Brau) have shown that yeast is able to propagate when ethylacetate is the sole source of carbon. M. Lindet (Annal de la brasserie, 1911) has studied the behavior of yeast in solutions of dextrose and laevulose, and finds that the dextrose is most easily fermented, while the laevulose serves better to build up the cells. P. Lindner and St. Cziser (Wochenschr. f. Brau., 1910) have made an exhaustive study of the assimilation of different carbohydrates by different yeasts. They find maltose is most suitable for assimilation, whereas lactose is assimilated only in rare instances. Dextrin is very often assimilated, but generally only to a slight extent. Saccharose is less important for the assimilation. Raffinose and fructose give only in rare cases a slight growth by assimilation. In many instances, the sugar is assimilated without being fermented; only in few cases is sugar fermented without being assimilated.

YEAST AUTOLYSIS

E. Navassart (Zeitschr. physiol. Chem.—70) says that sodium carbonate in concentration of 0.2 per cent. and potassium carbonate of 0.4 per cent. retard the autodigestion of yeast, as does also H. Cl. Kutscher and Lohmann (from the following paper by Takahashi and Yamamoto) find as products of the autolysis, Histidin, Lysin, Arginin, Leucin, Tyrosin, Asparaginic acid and ammonia, and T. Takahashi and T. Yamamoto find that the nitrogen substances of the press-juice are split up by autolysis into 30 per cent. di-amino acids and 70 per cent. mono-amino acids. It is the opinion of Lange that the dying off of the yeast during autolysis is not solely due to a dissolution of its body, but is to some extent caused by the action of the highly complicated molecules of the albumens. A. Harden and S. G. Paine (Proc. Chem. Soc., 1911) state that sodium chloride and ammonium sulphate in dezimolecular solutions are without influence upon the autolysis, but in molecular solutions they accelerate it. They obtained similar results with phosphates, arseniates, acetates, and citrates, and with the potassium salt of methyl-succinic acid. They suggest that this acceleration of the autolysis is most likely dependent upon the plasmolysing of the cell, which brings the glycogen into more intimate connection with the glycogenase.

PHYSICAL INFLUENCES AFFECTING YEAST

Clara Seisz (Ber. d. konig-Lehr f. Wien ohst. Gartenl.-Geisenheimer) has made comparative experiments to determine the influence of temperatures upon the growth and fermenting power of Saccharomyces apiculatus, ellipsoideus, etc., at temperatures from 12 to 18 C. The amount of alcohol produced is increased, but the large amount of CO_2 contained in the liquid has a retarding influence upon the fermentation. At a temperature of 27 C., there is decided shortening of the duration of a generation. The sensibility towards alcohol is quite different at differing temperatures; this is most plainly seen at temperatures of 34–36 C., when the yeasts mentioned grow considerably, but cause very little fermentation. F. Resenscheck has found by subjecting yeast juice to electrolysis that at the two opposite

poles there is a decided difference in the fermenting power of the juice. He accounts for the fact that the fermenting agent does not travel in toto to one of the poles, by suggesting the action of more than one enzyme. Slator (Journ. of Inst. of Brewing, 1911) claims that the rate of fermentation is proportional to the amount of yeast up to a concentration of 150,000,000 cells in 1 cc, and that the amount of sugar in solution has no influence upon it, when not too concentrated. Dextrose, laevulose, saccharose and maltose, are all fermented at practically the same rate, and there is no periodicity. The influence of temperature is great; at 20 C. dextrose is fermented 3.8 times as quickly as at 10 C. At 40 C., the fermentation is 1.6 times as quick as at 30 C. By calculation from the weight of one yeast cell, the author concludes that yeast ferments its own weight of sugar in slightly more than two hours at 30 C. M. Lubimenko and A. Troloff and Bagreief (Comps. rend d. l'acad. d. Sciences, 1912) have proved experimentally that wine yeast produces less CO_2 less alcohol and glycerine, but more acid, by fermentation in the light than in the dark; the amounts of esters are found to be the same. J. Gaule (Centrbl. f. physiolog., Bd—33) has shown that electric currents produced in a solenoide have a beneficial influence upon one of the enzymes in yeast, and Isillat and Sauton (Annal. de la brasserie et de la dist., 1909) have studied the influence of putrefaction gases upon the growth of yeast, and find that small amounts for short time action have a beneficial influence; but that higher concentrations and more prolonged exposure is detrimental. F. Hayduck, (Wochenschr. f. Br., 1910) in co-operation with J. Dehnicke and H. Wüstenfeld, has investigated the influence of air upon resting yeast, and concludes that resting yeast has a strong affinity for oxygen, which acts as a factor against its autolysis. He attributes this to the retarding influence of oxygen upon the action of endotryptase. The aeration of resting yeast is preservative of its fermenting power. Maumi and Warcollier (Comps. rend. de l'acad. des Sciences, 1910) have proved that rays from a mercury vapor quartz lamp will kill yeast in a $\frac{1}{4}$ mm layer of white Wine, within the course of five to ten seconds; but in apple wine from two to three minutes are required for the same action. From their experiments on the influence of ozone on different

organisms, H. Will and F. Wieninger (Zeitschr. f. d. ges. Brau., 1910) have found that 0.56 grm. ozone in one cubic centimetre air will kill 30,000,000 yeast cells inside one hour. With a larger number of cells, a slightly higher concentration is necessary. Schoenfeld and Krampf (Wochenschr. f. Br., 1911) have made a careful study of the influence upon pure yeast of warm cultivation and strong aeration and have formed the following conclusions: *Chemically,* (1) Higher amounts of albuminoids and ash; also larger amount of soluble phosphoric acid, mostly as organic phosphor compounds. (2) Smaller amounts of glycogen and soluble inorganic phosphor salts. *Physically*: Lower specific gravity; better clarification and agglomeration. *Physiologically*: Greater impetus, but lower fermenting power; less resistance to heat and extraction by water. This proves that the mode of cultivation has a determinating influence upon the chemical composition of yeast.

NON-POISONOUS INFLUENCES AFFECTING YEAST

Adam Dzierzbicki (Bull. Int. de l'acad. des Sciences Cracow, 1909) has studied the influence of humus from the soil upon yeasts and fermentation. In a solution of glucose, asparagin, and mineral salts, humus has a beneficial influence upon both growth and fermenting power of yeast, especially when the yeast is in very small amount. The action is not attributable to the nutritive value of humus, but is probaby analagous to the action of humus upon the azobacters and their assimilation of nitrogen. Speaking of the velocity with which the fermentation curve ascends, Martin Kochmann (Biochem. Zeitschr. 1909) finds that it is increased in presence of ethyl alcohol in concentrations of 0.2 per cent. to 0.3 per cent. He considers this a physiological process not an action upon the zymase, resulting in an acceleration of the production of the ferment. E. Kayser (Comps. rend. de l'acad. des Sciences, 1910) has made exhaustive experiments to prove that fermentation is quicker and more complete in the presence of 0.1 per cent. to 0.25 per cent. nitrate of manganese. For every yeast there is an optimum amount of this salt which lies between 3°/00 and 5°/00. Too large an amount of it stops the fermentation.

The action is stronger than that of potassium nitrate. In somewhat similar experiments, Fernbach and A. Lanzenberg (Compt. rend. de l'acad. des Sciences, 1910) have found that top yeast will start quicker when potassium nitrate is added in amounts up to two per cent. but its action on zymase shows no acceleration of the fermenting power in concentrations below 5°/00. Although it has a beneficial influence upon the fermentation, potassium nitrate has a pernicious influence upon yeast growth. P. Petit (Wochenschr. f. Brau., 1911) has made experiments which prove that washing yeast with phosphoric acid counteracts the weakening of the yeast frequently noticed where it is customary to use large amounts of raw grain. Oswald Schwarz (Biochem. Zeitschr., 1911) states that in the presence of suprarenin, yeast is able to ferment starch, glycogen, alanin, casein, with formation of CO_2. It has been shown by A. Harden and N. Young (Proc. Roy. Soc., London, 1911) that the fermentation of glucose, mannose and Fructose by yeast juice is accelerated by certain amounts of arseniate, and the action is noticeable a long time after the development of one equivalent of CO_2. The arseniate is present as such during the entire fermentation. Its action increases up to a certain concentration, and then decreases. In explanation of this fact, the authors say that the arseniates have an accelerating action upon the hexosephosphatase, thereby allowing a larger amount of phosphate to participate in the reaction. They add, · however, that in the fundamental reaction of the alcoholic fermentation, arseniates cannot take the place of phosphates. Arseniates also accelerate the autolysis, and the fermentation of glucose, provided there is an increased speed in the action of the diastatic enzyme Glycogenase.

ANTISEPTICS AND POISONS TO YEAST

F. Hayduck (Zeitschr. f. Angen. Chem., 1908) points out that the best method of separating that substance, poisonous to yeast, which is found in certain cereals, is extraction with 0.1 per cent. HCl. This extraction, after being neutralized with NaOH kills healthy yeast cells in a few minutes, in presence of sugar. The poisonous action is reduced to some extent by calcium salts.

Watery extracts produced from both brewers' yeast and pressed yeast, also have a similar toxic action.   Franz Duchacek (Biochem. Zeitschr., 1909) has found the influence of antiseptics upon yeast juice to be as follows: *Phenol.* 0.1 per cent. shows very little action. 0.5 per cent. reduces the fermenting power by 40 per cent. 1.2 per cent. stops the action of zymase entirely. *Chloroform.* 0.5 per cent. stimulates, while 0.8 per cent. has a very slightly weakening influence. 17 per cent. reduces the fermenting power by 64 per cent. *Chloralhydrate*—0.7 per cent. increases the fermenting power. 3.5 per cent. kills the zymase. *Benzoic and Salicylic acids* in dilutions of 0.1 per cent. have only very little weakening effect. 0.2 per cent. to 0.25 per cent. lower the fermenting capacity by 20 per cent. to 25 per cent. The author believes that all these antiseptics will, even where an increase in fermenting capacity is recorded, at first weaken the zymase, but later the endotryptase (or, as we now recognize it) the antiprotease is weakened and thus, indirectly, the zymase is strengthened. It is shown by F. Hayduck (Zeitschr. f. Spiritus industr, 1909) that distillery yeast, when dried quickly at high temperatures, produces by extraction with weak HCl. the substance poisonous towards bottom yeast while the same yeast, dried slowly at low temperatures, does not produce any poison. In this same connection, the same author (Wochenschr. f. Brau. 1910) after many further experiments comes to the following conclusions, regarding the yeast poison in cereals peptone and dried yeast. By precipitating a watery solution of peptone with $ZnSO_4$, there is ($ZnSO_4$) produced a sediment, which after separating the zinc-salt by dialysis, in the presence of sugar, acts as a poison upon yeast. The sediment produced by precipitating the dilute hydrochloric acid extraction from wheat flour with ammonium sulphate, after neutralization and dialysis, will act as a poison towards yeast. Similar precipitates may be produced from the extract of living yeast.   Maria Korsakow, (Berlin Deutsch. Botan. Geselsch 28) points out that sodium selenite has a poisonous influence upon zymase than upon reductase. Sodium selenite in concentrations of 0.5 per cent. increases the production of CO_2 by living yeast, and only becomes poisonous in higher concentrations.   The poisonous substance found by Hayduck in macerations of wheat

flour is not, according to A. Fernbach and E. Vulquin (Compt. rendu. l'acad. des Sciences, 151) indentical with the poison found by Fernbach in yeast macerations. The wheat flour maceration contains a volatile poison which, in the absence of sugar, retards the growth of yeast, while it is without influence upon the fermenting power. Besides the volatile poison, it contains a non-volatile substance which retards the action of zymase, but is without influence upon the growth of the yeast. The yeast maceration of Fernbach contains volatile substance, which retards the growth of yeast both in the absence and presence of sugar, but is without influence upon the zymase. E. Hailer (Zeitschr. fur Nahrungs genussmittel, 1911) has studied and proved the important fact that additions of grape sugar to the culture medium diminishes the toxic action of sulphurous acid upon yeasts. The action of SO_2 is stronger at 37 C. than at 22 C. 2.8 per cent. sodium sulphite has only a retarding influence upon the growth of yeast. Sodium bi-sulphite has a rather strong antiseptic action, but less strong than a sulphurous acid containing the same amount of sulphite. In isomolecular solutions, sulphurous acid has a stronger action than sulphuric acid and phenol. H. Luhrig and A. Sartori (Zeitschr. f. d. gesamt. Brau.) have demonstrated that in 100 cc. of 10 per cent. sugar solution, pitched with 2.5 grm. yeast, fermentation is *stopped* by: 75 mg. formic acid in case of invert sugar; 125 mg. formic acid,in case of glucose; 30 mg. benzoic acid in case of invert sugar; 125 mg. benzoic acid in case of glucose, and delayed by 90 mg. Pyrocatechin in case of invert sugar. H. Agulhorn (Compt. rend. de l'acad. des Sciences) points out that boric acid has only a slight poisonous action towards the yeast enzymes; some of them being rendered even more active by its addition. J. Baker and H. F. C. Hulton (Journ. Inst. of Brewing, 1910) have investigated the substances found in cereals, and compared them with the toxalbumines of animal life. They attribute the fact that press-yeasts have more resistance toward these poisons than brewers' yeast, to an acclimatization by continued cultivation in mashes containing the poisons. These latter are not affected by the malting process, nor weakened by heating the malt to 116 C., dry heat. Their action is considerably weakened, however, by

heating in water to 93 C. In further experiments with boric acid, Rosenblatt and Rosenband (Annal do l'Inst. Past) have found that the fermentation of a 1.25 per cent. saccharose solution in acid solutions is not retarded when a saturated boric acid solution is used, but is retarded by the use of saturated solutions of arsenius acid, succinic acid, and tartaric acid. Di-chloric-acetic acid stops fermentation in concentration of N/100. The determining factor in the action of acids upon the alcoholic fermentation is the concentration of the sugar solution. In saccharose solutions of 1.25 per cent. up to 5 per cent. the fermentation will be stopped by 0.98 per cent. H_2SO_4, 0.7 per cent, HNO_3, 3 per cent. acetic acid and 0.9 per cent. oxalic acid. In solutions of 10 per cent. it requires 1.96 per cent. H_2SO_4, 0.9 per cent. HNO_3, 12 per cent. acetic acid and 1.28 per cent. oxalic acid. Some further experiments by F. Hayduck (Wochenschr. f. Brau., 1909) tend to show that, contary to Fernbach, the toxic substance in yeast is never volatile, but always left intact in the residue from distillation P. Martinaud (Compt. rend. de l'acad. des Sciences) is in accord with Bioletti that, by the addition of sulphurous acid to must, a part combines with the sugar, and the remaining part restricts the fermentation. He claims that beer yeast cannot ferment a wort, or must, containing any free SO_2, and is of the opinion that when present in must, it is changed into SO_3 by certain species of Torula, prior to the normal fermentation. This opinion is controverted by Pozzi and Escot (Chemi. Centralblatt, 1910) who have shown that a number of yeast species have been acclimatized to grow and ferment in the presence of SO_2.

SPECIAL FERMENTATION PHENOMENA

In an interesting paper, J. Kudo (Centrallblatt f. Bact., 1909) points out that the fermenting power of yeast and yeast preparations is considerably restrained by the stomach juice, and accordingly yeast is acted upon in the same way, when passing through the alimentary canal of animals or human beings. He believes that the fermenting capacity of the intestines is only slightly increased by the use of yeast and yeast preparations and